

Calcium Reclamation and Synthesis of PCC For Acid Gas Control in Flue Gas

A Bachelors of Science Honors Thesis
Presented in Partial Fulfillment of the Requirements for
Graduation with Honors and Distinction from the
Department of Chemical and Biomolecular Engineering
At The Ohio State University

By
Imogen Mary Pryce

The Ohio State University

May 2006

Honors Thesis Committee:

Professor Liang-Shih Fan, Advisor
Professor Kurt Koelling

Approved by

Advisor

ABSTRACT

Fossil fuels currently play an invaluable role; accounting for over 80 % of the world's energy needs. The combustion of these fuels, however, generates the majority of anthropogenic acid gases, such as SO_2 and CO_2 . Thus, reducing emissions from fossil fuel conversion systems and stabilizing current levels of major pollutants in the atmosphere are essential to ensure the continued use of inexpensive fossil fuels while maintaining the delicate equilibrium in the environment. The increased number of natural disasters and the passage of major political programs, like the Clear Skies Act of 2003 and the Clean Air Act of 1990, highlight this need.

Post-combustion removal of SO_2 in flue gas can be achieved by contacting acidic SO_2 with alkaline sorbents such as limestone (CaCO_3), lime (CaO), and hydrated lime (Ca(OH)_2). The conventional flue gas desulfurization (FGD) processes are broadly classified as wet and dry processes and their overall conversions are about 90 % and 60 %, respectively. Considering the large quantity of Ca-bearing sorbents needed for FGD processes, the reclamation of unused Ca in these wastes is an attractive solution for improving the overall process economics.

In this project, various calcium sources are used to synthesize precipitated calcium carbonate (PCC) that has optimal morphological properties for both SO_2 and CO_2 capture from flue gas. First, different industrial wastes, Ca(OH)_2 , and CaCO_3 are procured and characterized for their Ca content. Various chelating agents are then used to promote the dissolution of solid samples. Based on the results of the calcium leaching tests, a common chelating agent, IDA, is selected for the subsequent investigation of PCC synthesis. It is found that IDA promotes the dissolution of Ca-bearing solids, while it does not interfere with the subsequent precipitation of PCC process. Finally, the effectiveness of PCC, produced with IDA, on SO_2 capture and CO_2 separation is investigated using a multi-gas thermal gravimetric analyzer.

To my family for their love and continual support.

ACKNOWLEDGEMENTS

I would like to thank Professor Liang-Shih Fan for allowing me this research opportunity, for welcoming me into his group, and for serving on my thesis defense committee. I would also like to express my gratitude to Professor Kurt Koelling for agreeing to serve on my thesis defense committee.

I would also like to express my sincere gratitude to Dr. Alissa Park for giving me the chance to do research in the group, for her confidence in my abilities, even when my own self-confidence faltered, for her technical expertise, and for becoming one of my very closest friends.

A great deal of thanks goes out to the other members of my research group who have helped me with various analyses and interpretations, especially Brittany Valentine and Shwetha Ramkumar, who spent endless amounts of time helping me in the lab. I would also like to express my gratitude to Mahesh Iyer and Luis Velasquez-Vargas for giving both their time and expertise when I most needed it. I would also like to thank Himanshu Gupta for sharing his technical knowledge, despite being hundreds of miles away.

I would also like to recognize my wonderful parents, Wendy Soucy, Jean-Marc Soucy, and David Pryce, for their support, love, and understanding. I also want to thank my siblings, Anneka, Philip, and Steven, for their love and for inspiring me with their creativity. I also extend a great deal of thanks to my roommates and best friends, Liza Toher and Erica Nollen, for their support, encouragement, and for keeping me sane. Last, but not least, I would like to thank my boyfriend, Nicholas Larusso, for being a continual source of strength and support and for being extremely understanding when things got stressful.

TABLE OF CONTENTS

ABSTRACT.....	I
DEDICATION.....	III
ACKNOWLEDGEMENTS.....	IV
LIST OF FIGURES	VI
LIST OF TABLES	VI
CHAPTER 1	1
INTRODUCTION.....	1
1.1 Sulfur Dioxide Emissions and Control Technologies	2
1.2 Carbon Dioxide Emissions and Separation Technologies	7
1.3 Project Objectives	9
CHAPTER 2 - EXPERIMENTAL METHODS	10
2.0 Safety.....	10
2.1 Solid Sample Analysis	11
2.2 Liquid Sample Analysis	13
2.3 Safety Considerations for Chelating Agents	15
CHAPTER 3 - PROCUREMENT AND CHARACTERIZATION OF INDUSTRIAL WASTES.....	18
3.1 Three Major Waste Products from a Coal Combustion Plant.....	19
3.2 Characterization of Procured Coal Combustion Products.....	22
3.3 Summary	27
CHAPTER 4 - CHELATION AND COMPLEXING AGENTS.....	28
4.1 Principle of Chelation.....	28
4.2 Potential Chelating Agents.....	29
4.3 Experimental Procedure	33
4.4 Results and Discussion.....	36
4.5 Summary	44
CHAPTER 5 - SYNTHESIS AND TESTING OF PCC	45
5.1 Introduction	45
5.2 Experimental Procedure	46
5.3 Results and Discussion.....	48
5.4 Summary	56
CHAPTER 6 - CONCLUSIONS AND RECOMMENDATIONS	57
REFERENCES	59

LIST OF FIGURES

Figure 1: SO ₂ emissions, 1983–2002 (US EPA, 2006).....	3
Figure 2: Calibration curve of Ca concentration vs. absorbance for flame atomic absorption spectroscopy	14
Figure 3: SEM images of FGD material at (a) 2 µm and (b) 1 µm	25
Figure 4: SEM images of fly ash at (a) 2 µm and (b) 1 µm	25
Figure 5: SEM images of bottom ash at (a) 2 µm and (b) 1 µm	25
Figure 6: Particle size distribution of procured FGD material.....	26
Figure 7: Calcium in solution over time from Ca(OH) ₂ at room temperature and pressure	37
Figure 8: pH vs. time for all chelating agents with Ca(OH) ₂ at room temperature and pressure..	38
Figure 9: Dissolution of Ca(OH) ₂ in acidic buffer solution with EDTA and IDA at room temperature and pressure.....	39
Figure 10: Effects of concentrations of chelating agents with Ca(OH) ₂ at room temperature and pressure.....	40
Figure 11: Effects of chelating agents with CaCO ₃ at room temperature and pressure.....	41
Figure 12: Effects of chelating agents with CaSO ₄ at room temperature and pressure.....	42
Figure 13: Effects of chelating agents with FGD at room temperature and pressure	43
Figure 14 - Schematic diagram of a slurry bubble column used for the synthesis of PCC (Gupta and Fan, 2002).....	46
Figure 15: Change of slurry pH over course of reaction, PCC generation from FGD.....	48
Figure 16: XRD spectrum for PCC made from Ca(OH) ₂ with IDA	50
Figure 17: XRD spectrum for PCC made from FGD with IDA	51
Figure 18: XRD spectrum for PCC made from FGD without IDA	52
Figure 19: SEM images of PCC made from Ca(OH) ₂ with IDA at (a) 2 µm and (b) 1 µm.....	53
Figure 20: SEM images of PCC made from FGD with IDA at (a) 2 µm and (b) 1 µm.....	53
Figure 21: SEM images of PCC made from FGD without IDA at 1 µm.....	53
Figure 22: Calcination and sulfation of PCC made from Ca(OH) ₂	55
Figure 23: Calcination and carbonation of PCC made from Ca(OH) ₂	56

LIST OF TABLES

Table 1: NFPA codes for selected chelating agents.....	17
Table 2: Typical FGD material compositions (adapted from TFHRC, 2005)	19
Table 3: Typical bottom ash composition (adapted from TFHRC, 2005)	21
Table 4: Typical fly ash composition (adapted from TFHRC, 2005)	22
Table 5: XRF data for calcium bearing solid samples	23
Table 6: Stability constants of various ligands (adapted from Morel, 1983).....	30
Table 7: Structures of selected chelating agents	32
Table 8: Required quantities of chelating agents for 0.01 M solutions.....	34

CHAPTER 1

INTRODUCTION

Fossil fuels currently play an invaluable role; accounting for over 80 % of the world's energy needs (Wolf et al, 2004). The combustion of these fuels, however, generates the majority of anthropogenic CO₂, H₂S, and SO₂. Thus, reducing emissions from fossil fuel conversion plants and stabilizing current levels of major pollutants in the atmosphere are essential to ensure the continued use of fossil fuels and to maintain the delicate equilibrium in the environment. This fragile balance can be jeopardized by the prevalence of such phenomena as acid rain from sulfur emissions. CO₂ emissions have been a major contributor to the "greenhouse effect," which is suspected to be largely responsible for the increased number of natural disasters. The passage of major political programs, like the Clear Skies Act of 2003 and the Clean Air Act of 1990, highlight the need for control strategies of these pollutants.

Specifically, the President's Clear Skies Act aims to cut sulfur dioxide emissions by 73 percent from the 11 million tons produced in the year 2000 to 4.5 million tons in 2010, with a cap of 3 million tons in 2018 (U.S. EPA, 2006). In order to continue using the vast majority of fossil fuels, especially coal, which is still available in abundant quantities in the United States, coal combustion plants have to impose much stricter regulations on their emissions. Given the ever-increasing requirements for emission control, the drive to make these technologies economically viable is pressing.

Both carbon and sulfur compounds are ubiquitous in natural environments. Their presence in fossil fuels is reasonable because for millions of years, coal and other materials have

been imperative in locking away carbon and sulfur to ensure that the natural balance of these materials is in check. Unfortunately, the widespread combustion of these carbonaceous materials has greatly increased the emissions of both carbon dioxide and sulfur dioxide into the atmosphere. Sulfur dioxide presented more serious immediate problems as the results of acid rain on human health, aquatic life, and climate change became evident (Smith et al., 2005). Anthropogenic carbon dioxide has also been the target of environmental concern; the general scientific consensus being that it is one of the major gaseous components of the “greenhouse effect.”

The relevance of sulfur dioxide and carbon dioxide emissions is highlighted and some of the control techniques are outlined in this chapter as an introduction to the objective of the work. The main objective of the project is to improve the overall efficiency of air pollution control systems through the reclamation of unreacted calcium used in flue gas desulfurization systems.

1.1 Sulfur Dioxide Emissions and Control Technologies

Sulfur dioxide in the atmosphere reacts by way of a number of factors, including temperature, humidity, and light, to form acidic mist. This matter settles out of the atmosphere through precipitation. Sulfur dioxide emissions undergo a series of reactions often ending up in the form of sulfuric acid and sulfate salts. These compounds are the aerosols that notoriously cause the hazy conditions around areas like Los Angeles (Manahan, 2000).

The build up of sulfuric acid eventually returns to earth via rain, snow, sleet, etc. Together, accumulations of sulfuric acid and nitric acid (from NO_x emissions) are more commonly referred to as acid rain. Acid rain, or acid deposition, has had significant environmental implications, including the acidification of soil and water, destroying plant and

aquatic life. In 1994, the average pH of acid deposition in the Northeastern United States was 4.4, ten times lower than pre-industrial, i.e. background, conditions (HBRF, 2001). This creates acidic conditions in soil and water, making ecosystems uninhabitable for plants and animals.

Given the effects that sulfur dioxide and its derivatives can have on the environment, it has become imperative that power plants, especially coal combustion plants, heavily regulate emissions. This regulation has generated a significant amount of interest in desulfurization technologies. Moreover, the national policies to reduce sulfur emissions, including the Clean Air Act and the Acid Rain Program, have helped lower emissions significantly since the early 1980's. Figure 1 shows that these emissions have decreased by 33 % and also highlights the major sources of sulfur dioxide emissions.

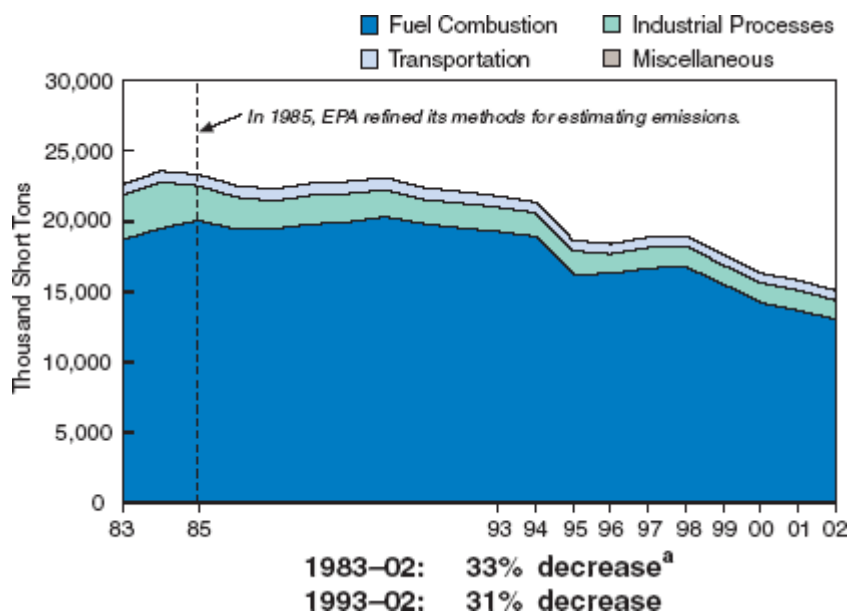
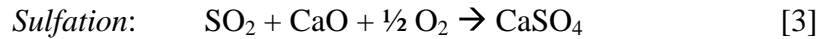
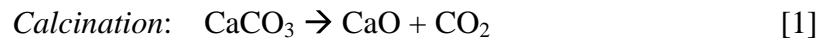


Figure 1: SO₂ emissions, 1983–2002 (US EPA, 2006)

A number of different techniques have been used to reduce SO₂ emissions. SO₂ control can be effectuated with either pre-combustion or post-combustion methods. Pre-combustion

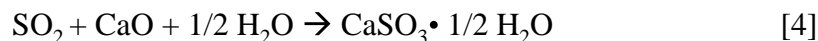
techniques focus on the removal of sulfur from coal, fuel switching, and blending of coals (both high sulfur-containing with low sulfur-containing). Post-combustion techniques involve using an additional step in the process and typically use chemical absorption to control the SO₂ emissions. The most common example is limestone wet scrubbing. Although another typical example is a spray atomizer dry scrubber, these systems currently do not have as high an overall efficiency as wet scrubber systems. Other techniques use adsorption principles to control the SO₂, such as dry-injection-type scrubbers. This type of scrubber, however, is still more costly and less effective than absorption based scrubbers (US EPA, 2006). Although only about 25 % of coal-fired power plants in the U.S. currently have FGD equipment, as regulations become more stringent, more and more plants will be required to install equipment (Fan and Jadhav, 2002).

The major distinction between types of FGD processes is whether a wet or dry flue gas desulfurization technique is used. Typically in dry FGD, the sorbent, e.g. CaCO₃ or Ca(OH)₂, is injected into the upper furnace region of the combustion system. It is referred to as the furnace sorbent injection (FSI) system. The sorbent can also be injected to the duct region after the air preheater or directly to the fluidized bed combustor (Fan and Jadhav, 2002). The reaction chemistries are given in Equations 1, 2 and 3.

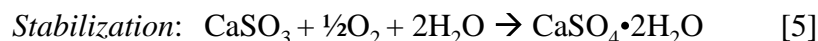


Both CaCO₃ and Ca(OH)₂ are calcined first as they are injected into the high temperature environment. Once they become CaO, the gas-solid sulfation reaction quickly takes place. In lime spray drying, another example of a dry FGD process, the SO₂ absorbed in the slurry reacts

with lime to form calcium sulfite (CaSO_3) in the reaction, as shown in Equation 4 (MacAdam and Parsons, 2004).



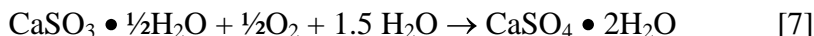
The majority of the CaSO_3 is then reacted with oxygen in the flue gas to stabilize it, forming calcium sulfate (CaSO_4), as shown in Equation 2.



Wet FGD processes generally involve the contacting of the SO_2 in the flue gas with an alkaline slurry. The chemistry is quite complex as it involves the dissolution kinetics of a number of compounds in water and the precipitation of reaction products (Fan and Radhav, 2002). Basically, in wet FGD processes, SO_2 absorbed in the slurry reacts with limestone to form calcium sulfite hemihydrate as shown in the reaction in Equation 3.



Carbon dioxide formed from reaction of limestone with SO_2 is released into the flue gas. Oxidizing air is bubbled through the slurry to convert $\text{CaSO}_3 \cdot 1/2 \text{H}_2\text{O}$ to gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) according to the reaction in Equation 4.



Typically, the calcium to sulfur ratio is in the range of 1.01 to 1.10 with a slurry pH of about 5 to 6. The best systems are capable of capturing 95 % of incoming sulfur dioxide, but the capital costs associated with this technology often corresponds to almost 20 % of the total plant cost. Moreover, there are environmental concerns with disposal of the waste products (Fan and Jadhav, 2002).

The research group at The Ohio State University has developed a patented process titled “the Ohio State Carbonation Ash Reactivation (OSCAR) process,” that produces engineered

PCC with controlled morphology that allows over 90 % sorbent conversion during an FSI application, i.e. without additional process equipment. Generally, the conversion of the calcium sorbents used in previous FSI systems is only about 50 %. Thus, more than twice of the stoichiometric requirement of sorbent is used to reduce the SO₂ emission to the appropriate level. The project showed that with improved sorbent morphological characteristics, the economics of the process is greatly improved. The process consisted of two parts: first, the generation of a highly reactive precipitated calcium carbonate (PCC); and second, the reaction of the PCC sorbent particles with SO₂ (Fan and Radhav, 2002). The PCC was designed with an increased pore size, allowing it to attain over 90 % conversion, versus the 50 % previously observed (Gupta and Fan, 2002). In addition, the OSCAR sorbents captured mercury and other trace heavy metals, which was an unexpected added improvement leading to multi-pollutant control.

Due to the excellent sorbent conversion of the OSCAR PCC (also known as supersorbent), new power plants are recommended to use the dry injection of the OSCAR sorbent to control SO₂. This technology is currently being commercially demonstrated in Canada. However, at this point commercial power plants utilize various other SO₂ control systems that have relatively low sorbent conversions ranging from 60 to 90 %. Due to low conversion, large quantities of sorbent need to flow through the system increasing both the capital and operating cost. In order to improve the overall efficiency of the current SO₂ capture technologies, the reclamation of Ca from the solid waste is proposed. At the end of the already installed SO₂ capture unit, unreacted Ca will be leached out using the proposed chemical activation method and the leached calcium will be reengineered as the OSCAR PCC which will be injected at the high temperature region of the combustion system to improve the overall sulfur capture efficiency. If the calcium can successfully be reclaimed from sorbent in current FGD

processes and converted to high reactivity OSCAR PCC, there is the potential not only to greatly reduce the sulfur capture cost but also to capture additional pollutants such as mercury and other trace heavy metals. Unlike previously demonstrated high efficiency systems, the OSCAR process does not require major capital equipment; consequently this technology can be easily implemented to the existing facilities.

1.2 Carbon Dioxide Emissions and Separation Technologies

Since the industrial revolution, the amount of carbon dioxide in the air has risen over 35 %. It is currently at 380 ppm and the scientific consensus is that this number will only increase (Lackner, 2006). Measurements of atmospheric carbon dioxide indicate that it is rising at a level of about 1 ppm per year. The climate effects of an increase in carbon dioxide are imminent; if current trends continue, the earth's surface temperature could easily raise 1.5-4.5°C (Manahan, 2000). This warming is in part due to the fact that carbon dioxide is one of the gases responsible for the "greenhouse effect." Although this phenomenon sparks debate in the scientific community, it is generally accepted that greenhouse gases, predominantly carbon dioxide, absorb infrared radiation preventing the earth from losing heat (Manahan, 2000). Effects of global warming and climate change are evident in the increasing number of natural disasters. Most recently, in the summer of 2005, overpowering hurricanes, particularly Rita and Katrina, had devastating effects on the southern part of the United States.

Currently, 80% of anthropogenic carbon dioxide is released in the combustion of fossil fuels. Moreover, half of the energy used in the United States comes from the use of coal (US DOE, 2006). As it is clear that there is yet an energy source that can effectively replace fossil

fuels, focus has been placed on removing and sequestering carbon dioxide from the effluent streams of combustion processes.

Although there are not yet strict regulations in place in the United States for reduction of carbon emissions, there has been precedent set by international efforts, such as the Kyoto Protocol, that indicates that the need for carbon sequestration technologies will become more important.

Carbon sequestration technologies have three main sections – capture, transport, and sequestration. One significant issue is that existing CO₂ separation technologies are not yet cost effective, and the overall economic feasibility of any carbon sequestration scheme often depends on the economics of the CO₂ separation technique. It is commonly accepted that capture can account for 50 % of the total cost of a carbon control system. The current industry standard uses amine absorbers and cryogenic coolers and costs approximately \$150 per ton of carbon. From an energy perspective, it has been proposed that adding CO₂ separation technology to an energy generation facility could cost on the order of 2.5 to 4 cents/kWh (US DOE, 2006). Given the need to develop cost effective technology, research efforts cover a broad set of potential solutions, including chemical and physical absorption or adsorption, low temperature distillation, gas separation membranes, mineralization and bio-mineralization.

The research group at The Ohio State University has also recently developed a novel PCC based system capable of 95 % conversion towards carbonation (Gupta and Fan, 2002). The group has also developed a multi-cyclic approach to carbon capture that has been highly successful. Reclamation of calcium from an FGD system for use in a carbon separation system would provide a valuable internal, less expensive, source of calcium for PCC based technology. PCC synthesized using recovered calcium from industrial waste can be used in both additional

SO₂ capture and CO₂ separation processes and this will help to improve the economic viability of the overall air pollution control scheme.

1.3 Project Objectives

Conventional FGD processes are broadly classified as wet and dry processes and their overall conversions are about 90 % and 60 %, respectively. Considering the large quantity of Ca-bearing sorbents needed for FGD processes, the reclamation of unused calcium in FGD waste and its conversion to OSCAR PCC is an attractive solution for improving the overall process economics and efficiency of sulfur control technologies. In addition, the OSCAR PCC synthesized from recovered calcium can be used as a CO₂ separation sorbent.

In this project, various calcium sources are used to synthesize precipitated calcium carbonate (PCC) that has optimal morphological properties for both SO₂ and CO₂ capture from flue gas. First, different industrial wastes are procured and characterized for their Ca content. Various chelating agents are then used to promote the dissolution of calcium in solid samples. Based on the results of the calcium leaching tests, suitable chelating agents are selected for the subsequent investigation of PCC synthesis. Finally, the chelating agent that most effectively leaches calcium from industrial waste while not inhibiting the precipitation of PCC is used in the generation of PCC. Being able to reclaim the unreacted calcium from FGD processes will be a crucial step in making the overall process more efficient and economically viable by providing sorbents for additional sulfur control and carbon separation.

CHAPTER 2

EXPERIMENTAL METHODS

Detailed experimental procedures are provided in later chapters, while the following sections describe safety precautions taken and the battery of characterization and analysis techniques used for both liquid and solid samples.

2.0 Safety

In order to characterize and assess the coal combustion products, it is necessary to dry the materials and then grind them to a powder. The by-products, though not dangerous materials, do present a respiratory hazard and, recognizing this, the materials are dried in a hood and a ventilation mask, goggles, and gloves are worn at all times during the preparation process. In the laboratory scale work with chelating agents, safety glasses and gloves are worn at all times. When working with finer powdered materials, a ventilation mask is also worn. When fabricating PCC, safety goggles and gloves are worn as personal protective equipment. The CO₂ gas cylinder is pressurized and consequently kept chained down at all times. For all the analysis work that is conducted, safety glasses and gloves are worn as minimum protection. In the analysis work that requires the use of pressurized cylinders, cylinders are chained down and stored securely.

2.1 Solid Sample Analysis

Particle Size Distribution

Particle size distribution (PSD) measurements are performed using a Micromeritics SediGraph 5100 instrument. Samples are prepared by first ensuring that they are an appropriate size, i.e. less than 250 microns. A slurry is prepared with 80 mL of water and 2.5 g of solid sample. At the beginning of each set of runs, a baseline analysis is made of the solvent, in this case distilled water. Between each sample the system is flushed to avoid cross-contamination. Once the instrument is cleaned and calibrated, the slurry is introduced to the system. X-rays are sent through the sample chamber and the particle size distribution (PSD) of the solid samples is determined based on the settling velocities of different size particles. The data is logged to a computer where it is analyzed and plotted in Micromeritics software.

X-Ray Diffraction

X-Ray Diffraction (XRD) is used to evaluate composition of materials and purity of samples. Equipment at the Campus Electron Optics Facility (CEOF) at The Ohio State University is used. Two diffractometers are used for analysis, the Scintag XDS 2000 and the Scintag PAD V. The PAD V is used when possible, however the XDS is necessary for some materials that are more easily analyzed in the vertical position of the XDS or for those that generate disruptive background in the PAD V. Samples are prepared in similar ways for both instruments. A sample of approximately 1 g or less is dried and ground and placed in the sample container. The appropriate 2θ range is selected. As the solid sample is exposed to X-ray at varying angles, different peaks appear at different angles. Both instruments log data to a central

server that is subsequently analyzed using EVA software. EVA is used to determine materials by matching the spectra in order to correctly identify solid samples.

Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) enables visual inspection of pore structure and high level imaging of materials. Two instruments are used in the CEOF at The Ohio State University. The Environmental SEM XL 30 (ESEM XL 30) allows for visualization of most samples. In some cases, it is useful to use the water atmosphere capabilities of the ESEM XL 30 to prevent dehydration or over-charging of the sample. Only a very small quantity of sample is needed for SEM work, typically on the order of several milligrams. The sample is vaporized to a stud and then gold coated. For samples with specific charging problems, different coatings can be used. This is explained in detail when it is required. For samples requiring higher magnification, the Sirion SEM is used. Samples are prepared the same way. For both SEMs, images are stored on a file server as they are captured.

X-Ray Fluorescence

Another method of analyzing composition of solid samples is X-Ray Fluorescence (XRF). The instrument used is a PANalytical Magi'X Pro Wavelength Dispersive XRF Spectrometer at the Materials Analysis Research Center (MARC) in Geological Sciences at The Ohio State University. This analysis involves a chemical digestion of samples and is completed by a trained technician.

Thermogravimetric Analyzer

Reactivity data is collected using a Perkin-Elmer Thermogravimetric Analyzer (TGA) (model TGA-7). A sample of approximately 10 mg is placed in a sample holder. Over the course of the run, the weight of the sample is collected at 10 s intervals. The sample is heated to calcination temperature at a given rate, while N₂ flows through the system. A switching mechanism allows for the subsequent introduction of the gas of interest, either CO₂ or SO₂. A more detailed description of this equipment and operating conditions has been published elsewhere (Iyer et al., 2004).

Brunauer-Emmett-Teller Analysis

Another method of physical characterization involved measuring the surface and pore properties of procured and synthesized solids using a low temperature N₂ absorption Brunauer-Emmett-Teller (BET) apparatus (NOVA 2200). The samples are weighed and then left to degasify for 6 hours in a nitrogen atmosphere at 250°C. The samples are subsequently analyzed for various physical characteristics, whilst being cooled in a bath of liquid nitrogen.

2.2 Liquid Sample Analysis

Flame Atomic Absorption Spectrometry

The spectrometer used is a Perkin-Elmer 1100 B Flame Atomic Absorption Spectrometer (flame AAS). The characteristic concentration for the flame AAS with a calcium lamp with a wavelength of 422.7 nm is 4 ppm and the linear range is 5 ppm, thus five calibration standards were prepared for 1 ppm to 5 ppm. Standards were prepared from a Perkin-Elmer stock standard of 1 µg/mL. Samples are diluted, when necessary, to be within this concentration range. An air-

acetylene flame is used for burning samples. Both gases are obtained from Praxair; air is zero grade and acetylene is grade 2.6 atomic absorption. Prior to each set of samples being analyzed, a calibration curve is obtained, an example of which is shown in Figure 2. Moreover, a check standard is measured every several samples to ensure that there is no alignment shift. In the case of elements that may cause interference, e.g. Si, spiked samples are run intermittently to verify that no shifting is occurring.

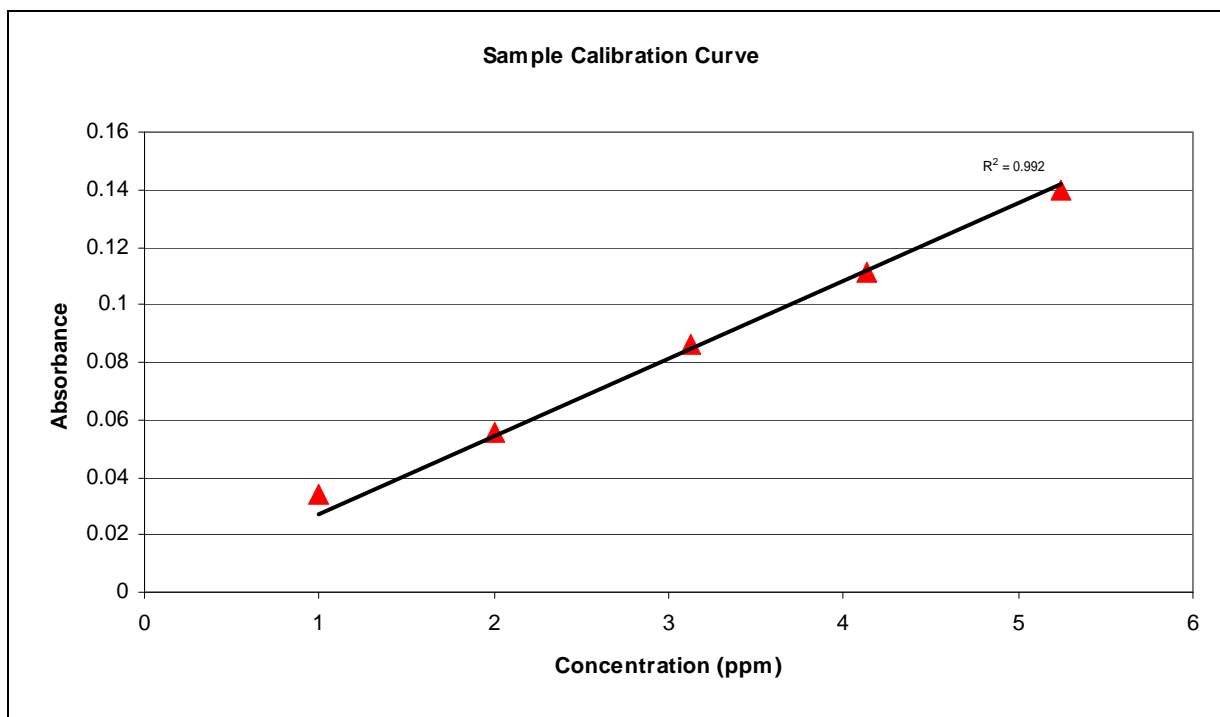


Figure 2: Calibration curve of Ca concentration vs. absorbance for flame atomic absorption spectroscopy

Inductively Coupled Plasma Optical Emission Spectrometry

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) is used to quantify calcium in the samples as a more reliable alternative to the flame AAS. The instrument used is a Perkin-Elmer Optima 3000 and is located in the MARC in Geological Sciences at The Ohio State University. Given that the samples emit as opposed to absorb, multiple emission lines can be chosen to increase the levels of calcium permissible in the samples. For the ICP-OES,

calibration standards are prepared from the stock solution at 20 ppm, 50 ppm, 100 ppm, 150 ppm, and 200 ppm. For samples with less calcium, the standards prepared for flame AAS are used. Argon is used to flush the system continuously. In all other regards, the operation of the instrument is similar to that described for operation of the flame AAS.

2.3 Safety Considerations for Chelating Agents

Understanding the safety elements of the chemicals in a process is of considerable importance for any chemical process. Therefore, each chelating agent should be evaluated to determine the safety implications that may arise if implemented in an industrial, or even lab, setting. The following information is for the chelating agents that were selected for further analysis (see Chapter 4) and was obtained from the Environment, Health, and Safety website at the Ohio State University (www.ehs.ohio-state.edu) and from the manufacturer supplied material safety data sheets (MSDS) for each chemical. The NFPA codes for the selected chelating agents are listed in Table 1.

EDTA

This substance is considered a hazardous substance according to OSHA 29 CFR 1910.1200. It is given a hazard alert code of “moderate.” It is stable and no hazardous reactivity is observed. It may be irritating to eyes and nasal passages, thus goggles are recommended and good ventilation is suggested.

IDA

This substance is considered a hazardous substance according to OSHA 29 CFR 1910.1200. It is given a hazard alert code of “moderate.” Iminodiacetic acid can cause eye and skin irritation. It may also cause respiratory and digestive tract irritation.

Picolinic Acid

Picolinic acid is considered a hazardous substance according to OSHA 29 CFR 1910.1200. There is limited evidence that suggests this substance may produce serious health damaged if ingested and may be a carcinogen. It is recommended that the dust is not breathed and any contaminated clothing is removed immediately.

Sodium Citrate

This substance is considered a hazardous substance according to OSHA 29 CFR 1910.1200. It does, however, have a “low” hazard alert code. Sodium citrate dihydrate is not regulated as a hazardous chemical, however is it is recognized as an eye and skin irritant. It may also cause respiratory and digestive tract irritation.

Sodium Metasilicate

This substance is considered a hazardous substance according to OSHA 29 CFR 1910.1200. It is given a hazard alert code of “high.” It should be noted that this is a corrosive substance and can cause serious burns to the eyes and skin, or the respiratory passages if inhaled. It has also been listed in the U.S. D.O.T. Appendix B of Marine Pollutants and Severe Marine Pollutants.

Sodium Triphosphate

This substance is considered a hazardous substance according to OSHA 29 CFR 1910.1200. It is given a hazard alert code of “moderate.” This substance causes respiratory tract irritation. It is also an irritant to the eyes and the skin. It may cause digestive irritation. It can also produce pulmonary edema if inhaled.

Table 1: NFPA codes for selected chelating agents

	EDTA	IDA	Picolinic Acid	Sodium Citrate	Sodium Metasilicate	Sodium Triphosphate
Health Hazard	1	0	2	0	3	1
Flammability	1	1	1	1	0	0
Instability	0	0	0	0	0	0

CHAPTER 3

PROCUREMENT AND CHARACTERIZATION OF INDUSTRIAL WASTES

There are a number of industrial waste streams produced in the traditional process of coal combustion. Using a novel calcium precipitation method, as described by Gupta and Fan, there is the possibility to convert these waste streams into valuable by-products, if the dissolution of calcium from these wastes can economically be carried out (Gupta and Fan, 2002). A method of using chelating agents to leach out calcium out of solid mixtures is proposed for this study. The stability of the coordinated calcium ions promotes the dissolution of Ca-bearing solids, and once calcium is dissolved into the liquid phase, it can be precipitated as OSCAR PCC. In this way, the waste streams that are currently considered expendable will become value-added by-products of the combustion and desulfurization processes.

This study will focus on the calcium leaching potential of wastes formed from Ohio coal and the surrounding areas, however the implications of this research should be applicable to products from coal combustion in all regions. Ohio coal samples tend to be mostly high sulfur bituminous coal, with fixed carbon percentages ranging from 46 to 66 % and ash contents ranging from 4 to 12 % (Manahan, 2000). The importance of coal composition should not be overlooked as it corresponds directly to the chemical and physical properties of the byproducts of interest.

3.1 Three Major Waste Products from a Coal Combustion Plant

There are a number of waste streams in the coal combustion process. The streams include fly ash, bottom ash, and flue gas desulfurization (FGD) material. These materials have limited applications in road base construction, i.e. stabilized base for concrete solutions, and in embankment construction (ACAA, 2005). Moreover, as previously mentioned, their properties are highly dependent on the coal from which they are produced, making it difficult to find accurate physical and/or chemical properties for the materials.

Nevertheless, properties have been compiled in an attempt to understand potential uses, specifically reclamation of calcium from these solid byproducts. Three different solid samples have been evaluated – FGD scrubber material, coal bottom ash, and coal fly ash.

FGD Scrubber Material

The composition of FGD scrubber material is dependent on both coal type and scrubbing process. Table 2 is taken from a study of FGD by the Turner-Fairbank Highway Research Center.

Table 2: Typical FGD material compositions (adapted from TFHRC, 2005)

Type of Coal	Sulfur Content	Type of Process	CaSO ₃	CaSO ₄	CaCO ₃
Bituminous	2.9 - 4.0	Lime - Wet	50 - 94	2 - 6	0 - 3
Bituminous	2.9	Limestone - Dry	19 - 23	15 - 32	4 - 42
Bituminous	1.0 - 4.0	Dual Alkali (Ca-Na) - Wet	65 - 90	5 - 25	2 - 10
Bituminous	2.0 - 3.0	Lime (Forced Oxidation) - Wet	0 - 3	52 - 65	2 - 5

As is evident from the table, the quantity of calcium used in the FGD process is very large, however once they are reacted, the sulfur-rich products, calcium sulfate and calcium sulfite, often dominate the composition of the reacted solids. The only calcium that is “reclaimable” at

this point may be the calcium carbonate. Consequently, the limestone process seems most appealing for our application. In addition, the focus has been limited to bituminous coals because of their predominance in Ohio. The physical properties are varied to a similar degree. They are influenced by the way in which the materials are treated. For stabilized FGD scrubber material, the specific gravity is expected to be between 2.25 and 2.60. The wet density is between 1,460 and 1,780 kg/m³, while the dry density is expected to be 1,210 to 1,540 kg/m³. Solids are expected to account for 55 to 80 % of total content. The current usage rate of the waste FGD materials produced in wet and dry scrubbers is only about 8 % (ACAA, 2005).

Bottom Ash/Slag

Bottom ash and bottom slag are often grouped together for classification purposes. They differ as a result of type of furnace used to burn the coal. Both are collected from the base of the furnace and are typically coarse, granular, and incombustible. This analysis will focus on bottom ash, as opposed to slag, because it comes from the most common type of coal burning furnace, a dry-bottomed pulverized coal burner.

The physical properties of bottom ash are mostly dependent on chemical composition; the carbon content, for example, greatly influences the specific gravity, which ranges from 2.1 to 2.7 (TFHRC, 2005). Table 3 is an excerpt from a study by the Turner-Fairbank Highway Research Center.

Table 3: Typical bottom ash composition (adapted from TFHRC, 2005)

Coal Type:	Bituminous		
Location	West Virginia		Ohio
SiO ₂	53.6	45.9	47.1
Al ₂ O ₃	28.3	25.1	28.3
Fe ₂ O ₃	5.8	14.3	10.7
CaO	0.4	1.4	0.4
MgO	4.2	5.2	5.2
Na ₂ O	1.0	0.7	0.8
K ₂ O	0.3	0.2	0.2

The calcium content in this type of material is anticipated to be fairly low, however, testing is necessary, because it will be dependent on specific coal type. This data has been limited to bituminous coal, because of its prevalence in Ohio.

Fly Ash

The third material type to be examined is coal fly ash. Fly ash is a fine material that is carried in the flue gas and typically removed by an electrostatic precipitator, a bag house, or a type of cyclone. It is made up of spherical particles with a typical size distribution, for bituminous coals, of less than 0.075 mm. The specific gravity ranges from 2.1 to 3, while specific surface area ranges from 170 to 1000 m²/kg (TFHRC, 2005). The type of coal burned substantially affects chemical properties, although, typically, the main components are silica, alumina, iron oxide, calcium, and carbon. Table 4 is from a study by the Turner-Fairbank Highway Research Center gives the normal ranges for chemical composition of fly ash (TFHRC, 2005). The amount of calcium in this material must also be tested given the particularly large potential range, 1-12 %.

Table 4: Typical fly ash composition (adapted from TFHRC, 2005)

Component	Bituminous
SiO ₂	20-60
Al ₂ O ₃	5-35
Fe ₂ O ₃	10-40
CaO	1-12
MgO	0-5
SO ₃	0-4
Na ₂ O	0-4
K ₂ O	0-3
LOI	0-15

3.2 Characterization of Procured Coal Combustion Products

Coal combustion products (CCPs) were procured from American Electric Power (AEP) Service Corporation in Lancaster, Ohio. The samples came from the John E. Amos Plant in St. Albans, West Virginia. The three samples procured were stabilized scrubber by-product, i.e. FGD material from a wet FGD process, fly ash, and bottom ash.

The CCPs – fly ash, bottom ash, and FGD material – were extensively characterized to understand how they could be better utilized for carbonation and sulfation. Chemically, the emphasis was placed on evaluation the homogeneity of the material, the amount of calcium, and also the type of calcium compounds that had formed. X-Ray Diffraction (XRD) and X-Ray Fluorescence Spectrometry (XRF) were used for the chemical analysis. The samples were analyzed physically to determine specific physical characteristics of the materials using pore size determination (PSD) techniques, BET, and through scanning electron microscopy (SEM).

Chemical Composition

The chemical composition of the samples was determined using XRF. The data are summarized in Table 5. The remaining weight percentages are attributed to carbon.

Table 5: XRF data for calcium bearing solid samples**FGD**

Compound	Wt%
SiO ₂	2.59
Al ₂ O ₃	1.50
Fe ₂ O ₃	1.49
MgO	0.78
CaO	9.56
SO ₃	12.55

Element	Wt %
Si	1.21
Al	0.80
Fe	1.04
Mg	0.47
Ca	6.84
Sx	5.03

Bottom Ash

Compound	Wt%
SiO ₂	8.33
Al ₂ O ₃	6.11
Fe ₂ O ₃	0.62
MgO	0.14
CaO	0.09
S	0.05

Element	Wt %
Si	3.90
Al	3.23
Fe	0.43
Mg	0.09
Ca	0.07
S	0.05

Fly Ash

Compound	Wt%
SiO ₂	32.55
Al ₂ O ₃	19.84
Fe ₂ O ₃	2.08
MgO	0.54
CaO	0.48
SO ₃	0.34

Element	Wt %
Si	15.22
Al	10.50
Fe	1.45
Mg	0.33
Ca	0.35
Sx	0.14

As is evident, the only significant source of calcium is the FGD material among three solid samples procured for this study. The calcium oxide percentages in the fly ash and the bottom ash are approximately 1 % and 0.5 %, respectively. This does not represent a sufficient amount to seriously consider using for PCC synthesis to be used in CO₂ or SO₂ capture processes. Therefore, it was decided that future analysis and experiments would proceed using only FGD materials. Unfortunately, no material from a dry FGD process could be procured. This material would, presumably, have had the highest calcium content.

XRD data was also collected for the samples. The data for the materials was obtained but is not shown. It was rather difficult to distinguish peaks for each compound in the solid samples

because of the heterogeneity of the samples. Moreover, the diffractometer can only measure a small sample of the given material and, especially in the case of such mixed samples, presents reliability issues.

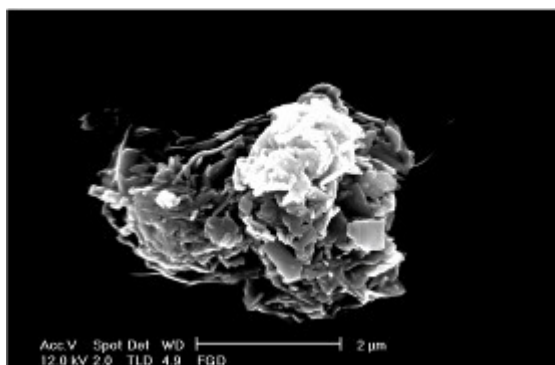
Physical Characteristics

Given the relatively low amount of calcium in fly ash and bottom ash, only some of the physical composition data is presented. All of the physical composition data for FGD material is shown.

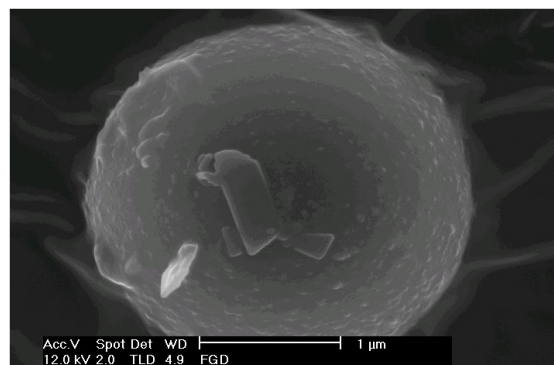
In order to obtain high quality SEM pictures of the materials, the samples were dried and coated with osmium plasma. Initially, the samples were coated with gold, but, given the relative fineness of the particles, the charging of the particles distorted the images significantly. The osmium-coated samples were analyzed using a Sirion SEM. The images of the FGD material are shown in Figures 3 (a) and (b).

Although some particles in the sample are spherical, the material was dominated by the presence of plate-like material. From Figures 3 (a) and (b), the plate-like shapes of FGD may contribute to a higher surface area. Aggregated compounds, like that shown in the figure, were prevalent throughout the sample. At higher resolution it became evident that there were also spherical species present, as shown in Figure 3 (b). Similar spherical species were present in both the bottom ash and the fly ash samples, as shown in Figures 4 (b) and 5 (b).

Aggregated compounds were also present in the bottom ash and fly ash; however, they were not composed of the same type of plate-like compounds seen in FGD. Instead, they appeared to be more amorphous, as seen in Figures 4 (a) and 5 (a). In the case of the fly ash, smaller spherical particles are also observable in particle clusters; see Figure 4 (a).

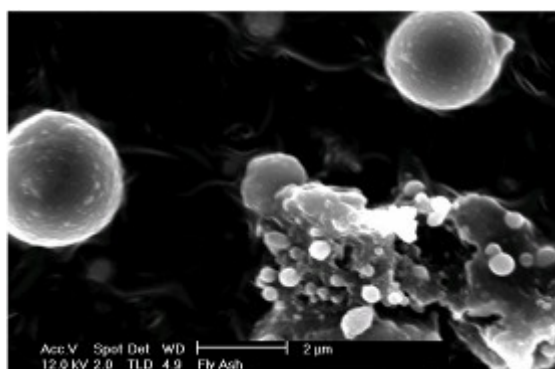


(a)

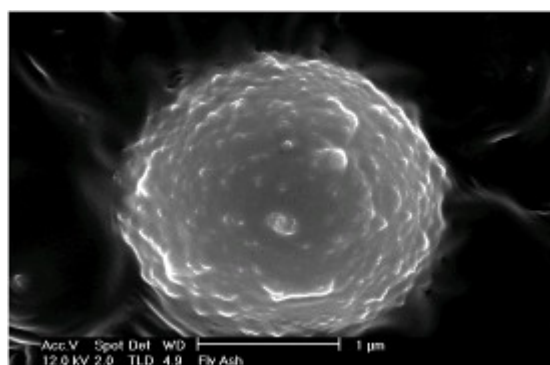


(b)

Figure 3: SEM images of FGD material at (a) 2 μm and (b) 1 μm

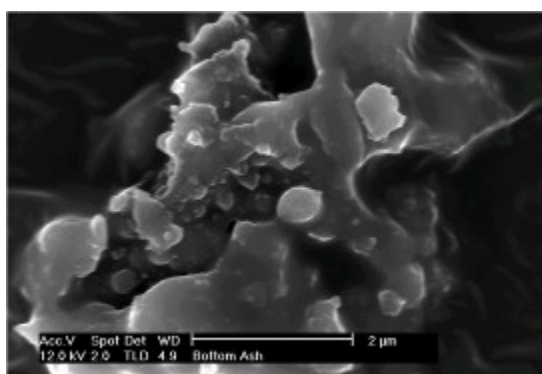


(a)

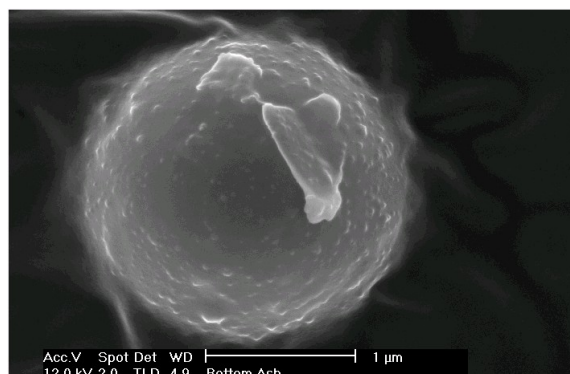


(b)

Figure 4: SEM images of fly ash at (a) 2 μm and (b) 1 μm



(a)



(b)

Figure 5: SEM images of bottom ash at (a) 2 μm and (b) 1 μm

Before using the FGD material in any tests, the material was ground and sieved to less than 250 μm . The seclusion of larger particles was to ensure that the calcium was adequately available to the chelating agent, and to keep the same PSD in initial solid samples throughout the dissolution experiments. Different PSDs of the initial materials would lead to varied mass transfer problem between experimental runs. The PSD for the sieved FGD material is shown in Figure 6. The average particle size was approximately 35 μm and the distribution mostly follows a normal distribution curve. The density of the FGD material was 1.78 g/cm^3 .

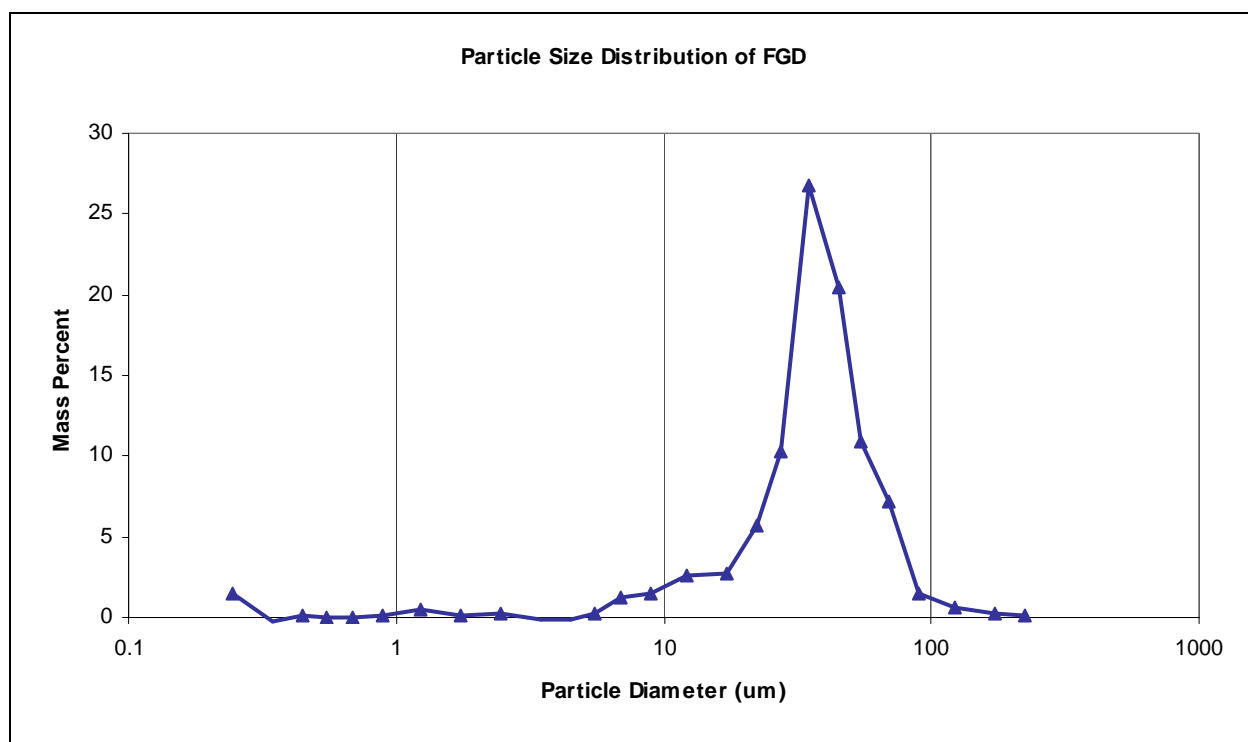


Figure 6: Particle size distribution of procured FGD material

3.3 Summary

From the chemical analysis of the industrial waste, FGD material was the most viable option for the proposed calcium reclamation study. The physical characteristics, particularly the SEM images, of the samples showed the differences in the structural properties of the samples being evaluated. The agglomerated plate-like structure of the FGD material in the SEM images may be indicative of the sulfate formation or material that is readily available for calcium reclamation. Either way, the surface area of this material appears to be greater than the alternative materials, a property that can be used to the advantage of the dissolution process or, in other words, the ease with which a chelating agent can uncover and leach out the calcium ions. The subsequent step of the work will attempt to identify chelating agents that could be used to leach calcium from FGD materials, but do not inhibit the formation of PCC in the PCC generation process.

CHAPTER 4

CHELATION AND COMPLEXING AGENTS

The main objective of this work is to reduce the amount of calcium sorbent required for sulfur control, and to use the OSCAR PCC synthesized using reclaimed calcium from the industrial wastes for both additional SO₂ capture and CO₂ separation from a flue gas stream. There are two ways in which this can effectively be achieved, the conversion of the sorbent can be increased or calcium from sorbents in existing systems can be reclaimed. This reclaimed calcium can be used to produce higher efficiency calcium-based sorbents (OSCAR PCC), ultimately reducing the amount of material flow by the direct injection of reinvented PCC into the combustor. This work focuses on the leaching of calcium from utilized sorbents. In order to be able to leach the ions from these solids, a chemical additive is required. This chapter focuses on the use of chelating agents as potential candidates for complexing unused calcium in order to promote the dissolution of Ca-bearing industrial wastes.

4.1 Principle of Chelation

Chelating agents are typically used to form complexes with metal ions. Polydentate ligands are often preferred because of their capacity to bind metal ions at multiple sites; moreover they are able to form multiple species with the metal ions, thus increasing solubility (Morel, 1983). Ligands that are smaller, i.e. monodentate and bidentate ligands, can be advantageous because they have the ability to leach ions out of more tightly packed compounds. Because of the way in which a chelating agent “hides” the metal ion, these ligands are sometimes

referred to as *sequestering agents* (Brown et al., 1991). Complex formation typically occurs because of a favorable entropy change in the system. This entropy increase results because as the metal ions are complexed out of a chemical compound, the molecules that they were bound to are released into the system. The increase in number of species in the system increases the entropy, i.e. disorder, of the system (Brown et al., 1991).

4.2 Potential Chelating Agents

Chelating agents have been used in a number of industries to remove metals from solution. The proposed technique of calcium dissolution borrows from those applications. Specific examples include the leaching of calcium in the pulping industry to prevent fouling from the precipitated calcium and other metallic salts (Sillanpaa et al., 2001), and dissolution of calcium to prevent scale formation that results in fouling of membranes and heat exchangers in a number of industries (Chong and Sheikholeslami, 2001 and MacAdam and Parsons, 2004). In the pulping industry the concentrations of EDTA and DTPA, another chelating agent, used are both approximately 100 μM (Sillanpaa et al., 2001). Recent studies even show previously ignored implications of chelating agents in biological systems (Friis et al., 2003). The dissolution rates of calcium carbonates and other calcium compounds have been shown to increase greatly with the addition of chelators to solution. The most studied of these compounds is undoubtedly ethylenediaminetetraacetic acid (EDTA). Even at remarkably low concentrations, 1-10 mM EDTA, dissolution rates increase by as much as 1 order of magnitude (Perry et al, 2004). As expected, Fredd and Fogler showed that dissolution rates are affected not only by chelating agent, but also by pH (Fredd and Fogler, 1998). They studied extensively the dissolution of calcite with the chelating agents, 1,2-cyclohexanediaminetetraacetic acid (CDTA), diethylenediamine

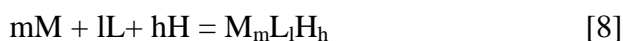
pentaacetic acid (DTPA), and EDTA at both different concentrations and different pH levels. It follows from the definition of a chelating agent that pH would have a significant effect because of the combined effects of the hydrogen ions in solution, the chelating reactions, and the water reaction. Fredd and Fogler confirmed this over the pH range 4-12.

The stability constants of selected chelating agents, as reported by Morel in his book, Aquatic Chemistry, are included in Table 6.

Table 6: Stability constants of various ligands (adapted from Morel, 1983)

Ligand	Ca ²⁺	Stability Constant
IDA	CaL	3.5
Desferrioxamine	CaL	3.5
Picolinate	CaL₂	3.8
SiO₃²⁻	CaL	4.2
SO ₄ ²⁻	CaL ₂ .s	4.62
Citrate	CaL	4.7
OH	CaL ₂ .s	5.19
PO ₄ ³⁻	CaL	6.5
Malonate	CaHL	6.6
P ₂ O ₇ ⁴⁻	CaL	6.8
P₃O₁₀⁵⁻	CaL	8.1
CO ₃ ²⁻	CaL.s	8.22
CO ₃ ²⁻	CaL.s	8.35
P ₂ O ₇ ⁴⁻	CaOHL	8.9
Citrate	CaHL	9.5
F ⁻	CaL ₂ .s	10.4
P₃O₁₀⁵⁻	CaOHL	10.4
CO ₃ ²⁻	CaHL	11.59
Citrate	CaH₂L	12.3
EDTA	CaL	12.4
P ₂ O ₇ ⁴⁻	CaHL	13.4
SiO₃²⁻	CaHL	14.1
P₃O₁₀⁵⁻	CaHL	14.1

The stability constants given in the table correspond to the β value of the reaction, described in Equations 7 and 8.

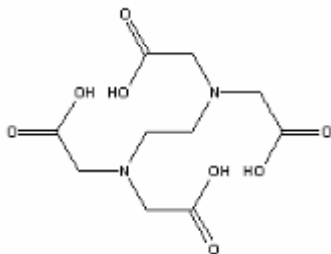
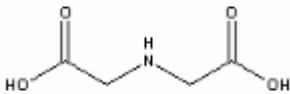
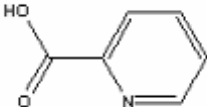
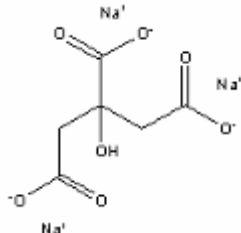
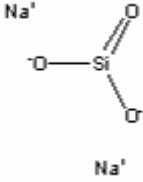
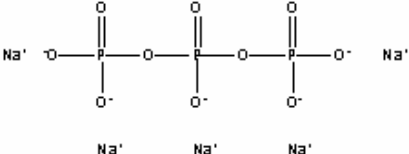


$$\beta_{mlh} = (M_m L_l H_h) / (M)^m (L)^l (H)^h \quad [9]$$

The chelating agents chosen are those whose stability constants are similar to that of CaCO_3 , at relative stability of 8.22 and 8.35, to ensure that the calcium ion complexation can occur when in appropriate solution. It is expected that those with higher stability constants will be more successful in dissolving Ca-bearing solid samples. Ions that form solids with calcium are indicated by a “.s” following the Ca^{2+} type molecule that forms. For reference, the stability constant of CaCO_3 has some variability depending on the type of carbonate solid formed, e.g. vaterite, calcite, etc. These ligands are highlighted on the table.

From this initial list, six chelating agents were chosen. It is also expected that the ligands with higher stability constants would potentially inhibit the precipitation of calcium carbonate. Thus, the list of chelating agents was selected such that stability constants did not deviate too greatly from the stability constants of CO_3^{2-} ions with respect to calcium ions. Moreover, they were chemicals that are readily available and not prohibitively expensive. The list consists of: immunodiacetic acid (IDA), picolinic acid (Picolinate), sodium metasilicate, sodium citrate dihydrate, sodium triphosphate, and EDTA. They are in bold-faced type in Table 6. The chemical structures of these chelating agents are shown in Table 7.

Table 7: Structures of selected chelating agents

Chelating Agent	Number of Chelation Sites	Structure
EDTA	4	
IDA	3	
Picolinic Acid	1	
Sodium Citrate	3	
Sodium Metasilicate	2	
Sodium Triphosphate	5	

Interestingly, a study by Westin and Rasmuson found that the type of chelating agent, i.e. EDTA and citrate, directly impacted both the particle size and shape of calcium carbonate that precipitated from solution (Westin and Rasmuson, 2003). Not surprisingly, they found that the particle concentration was reduced for a solution with EDTA or citrate. Moreover, they found that average particle size was lowered in the presence of chelating agents. They found that solutions with EDTA formed mostly spherical shapes, suggesting the vaterite form of CaCO_3 , while citrate caused the formation of rhombi structured particles, indicating calcite. These results may provide an important key to eventually understanding how calcium complexes can be regenerated to form calcium carbonate.

Another study that focused on scale formation in heat exchangers, evaluated the effects of CaSO_4 on the precipitation of CaCO_3 . Their observations suggest that the presence of CaSO_4 , in the range of 0.002 to 0.01 M, increases the solubility of CaCO_3 by more than an order of magnitude and reduces the formation of scale and, hence, the fouling of heat exchanger equipment. This is an interesting point given the significant amount of CaSO_4 in the products to be tested. More importantly, the potential for change in reaction kinetics, etc., due to the “contamination” of the carbonate of interest should be considered over the course of the experimental analysis.

4.3 Experimental Procedure

Screening Tests

Initial screening test were performed to test the efficacy of the proposed chelating agents – EDTA, IDA, Picolinic Acid, Sodium Citrate, Sodium Metasilicate, and Sodium Triphosphate. Disodium EDTA, reagent grade, was obtained from GFS Chemicals. IDA, disodium salt, 1-

hydrate, was procured from Acros Organics. Picolinic acid was obtained from ACROS Organics at 99 % purity. Sodium citrate was enzyme grade from Fisher Scientific. The sodium triphosphate was laboratory grade from Fisher Scientific. Sodium metasilicate, nonahydrate ACS reagent grade, was procured from MP Biomedicals, Inc.

From the literature, it is evident that chelating agents, specifically EDTA, are used in very small quantities, i.e. the micro- to milli-molar scale. Consequently, the initial round of experiments used 0.01 M of each chelating agent. Using a conservative amount, the intention was to determine which chelating agents could be discarded immediately and which had potential for further investigation.

Each test was run in a 250 mL “reactor.” Table 8 corresponds to the amount of chelating agents required for a 0.01 M solution in 250 mL.

Table 8: Required quantities of chelating agents for 0.01 M solutions

Chelating Agent	Molecular Weight	Amount (g)
EDTA, disodium salt	372.24	0.9306
IDA, disodium salt	195.08	0.4877
Picolinic Acid	123.11	0.3078
Sodium Citrate Dihydrate	294.10	0.7353
Sodium Metasilicate	122.06	0.3050
Sodium Triphosphate	367.93	0.9198

In the screening experiments, the chelating agents were tested with calcium hydroxide, Ca(OH)_2 , rather than FGD solid samples in order to minimize the factors affecting the dissolution rate. The amount of Ca(OH)_2 used in each case was 1 g. Compared to the amount of chelating agent, this solution was supersaturated, as it is equivalent to 0.05 M Ca^{2+} , however, some of the chelating agents are polydentate and would be able to complex more than once with Ca ions. The reactions were allowed to run for 2 hours while being continuously stirred with a magnetic stir bar at 900 Hz. Samples of the solution were taken periodically and filtered using

FisherBrand 0.2 μm nylon filters. All solution samples were then analyzed for calcium concentration in the collected liquid samples using flame AAS as described in Chapter 2.

Effect of pH on the dissolution rate

Once the number of chelating agents had been refined, the importance of pH to the solutions was tested for the two selected ligands. A low pH buffer solution was prepared from glacial acetic acid from FisherChemicals and sodium acetate, also from FisherChemicals. This provided a solution that was slightly acidic, pH of 4.74, directly contrasting the basic solution that would form with calcium sorbents, especially calcium hydroxide. In order to have appropriate strength, the buffer solution was made of 0.5 M acetic acid. The two most successful chelating agents determined from the screening tests were used at 0.01 M with the buffer solution. Once again, 1 g of calcium hydroxide was used in a 250 mL reactor. The plan was to run the experiments for 1 hour or until complete dissolution, which with an acidic solution would be much faster. The samples obtained periodically were analyzed using ICP OES; the procedure for which is described in Chapter 2.

Effects of concentrations of chelating agents on the dissolution rate

The concentration sensitivity of the chelating agents was evaluated by choosing the two best chelating agents and testing at half and two-fold quantities, i.e. 0.005 M and 0.02 M. This was to develop an understanding of the level of chelating agent required. Similar to the buffer testing, these tests were run for 1 hour, after which time it was assumed the concentrations would have leveled off.

Effects of material sensitivity on the dissolution rate

In order to choose the best chelating agent it was important to expand the scope of the dissolution work beyond Ca(OH)_2 , especially given that the hydroxide is already partially soluble in water. In particular, the most promising chelating agents were tested versus CaCO_3 and CaSO_4 . These compounds are chosen because they are the forms of calcium compounds often found in many industrial wastes. In addition, FGD was tested as the industrial standard, i.e. non-laboratory grade material; it was procured as described in Chapter 2. Each material test was run with 0.01 M chelating agent and was left to run for the duration of 2 hours, with samples taken periodically. The liquid samples were analyzed for calcium content using ICP OES.

Note that all the experiments in this study were performed under ambient temperature and pressure.

4.4 Results and Discussion

In the screening tests previously outlined, the objective was to determine the compound that was the most effective at chelating, or leaching, the calcium ions from the calcium hydroxide solid sample and into solution. As is evident in Figure 7, EDTA and IDA are the two of the best chelating agents for leaching calcium from Ca(OH)_2 . Chelating agents with less calcium leached into solution than water are not shown on the graph; these were sodium metasilicate, sodium triphosphate, and sodium citrate. Although picolinic acid is also notable, IDA was chosen for further investigation over picolinic acid because of its overall performance and because IDA is a safer chemical to handle. Referring back to the safety data in Chapter 2 (section 2.3), picolinic acid has a health hazard rating of 2, while that for IDA is 0.

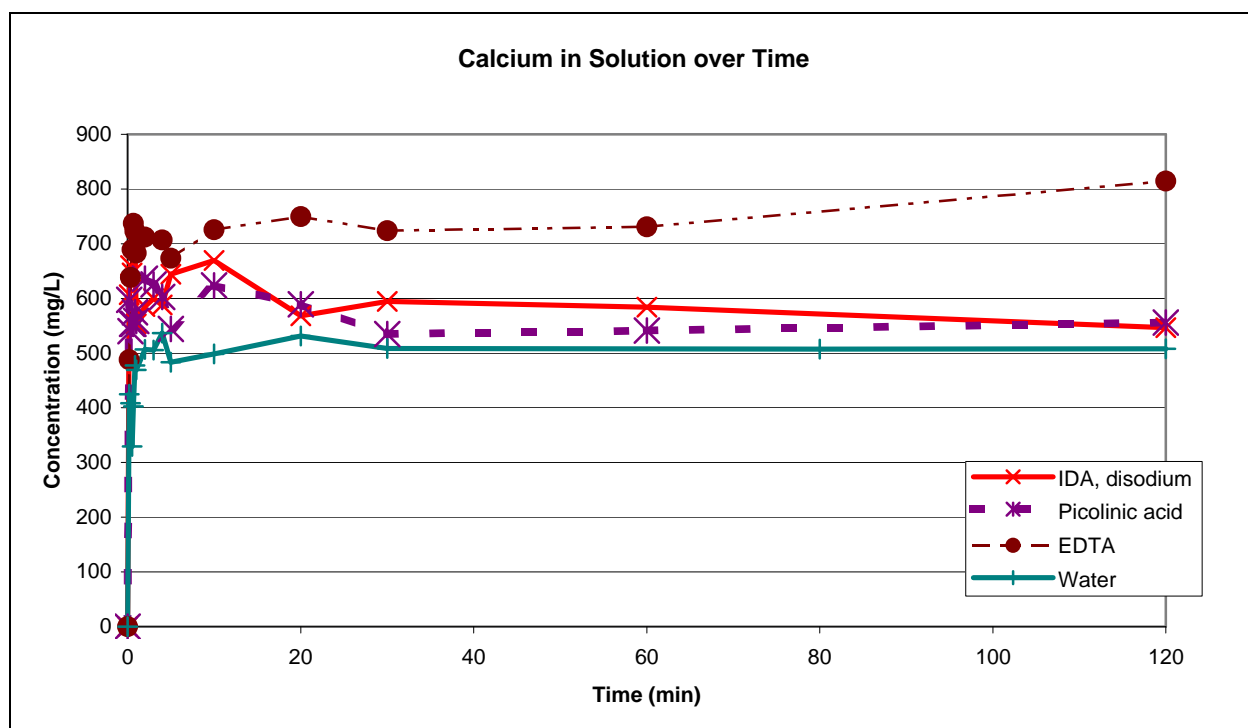


Figure 7: Calcium in solution over time from $\text{Ca}(\text{OH})_2$ at room temperature and pressure

A noteworthy point to make is that, although the samples were filtered before being placed in sample containers, in some cases, a small amount of solids were found at the bottom of the sample bottles the following day. For the EDTA solution, solids formed in the samples taken in the first ten minutes, consequently, the data shown above may be slightly skewed. From twenty minutes onward, however, no solids formed and the data can be considered more reliable. The final concentration of calcium was 815 ppm. In the case of IDA, solids did not form at any time. The final concentration of the solution with IDA was 547 ppm.

For all experiments, the pH was monitored. As a result of the overpowering causticity of $\text{Ca}(\text{OH})_2$ in solution, the pH level jumped to 12 almost immediately in all instances, including with picolinic acid, see Figure 8. The pH of the slurry did not change through each run and this eliminates the possibility of pH effect on the dissolution of Ca-bearing solid samples for this set of experiments.

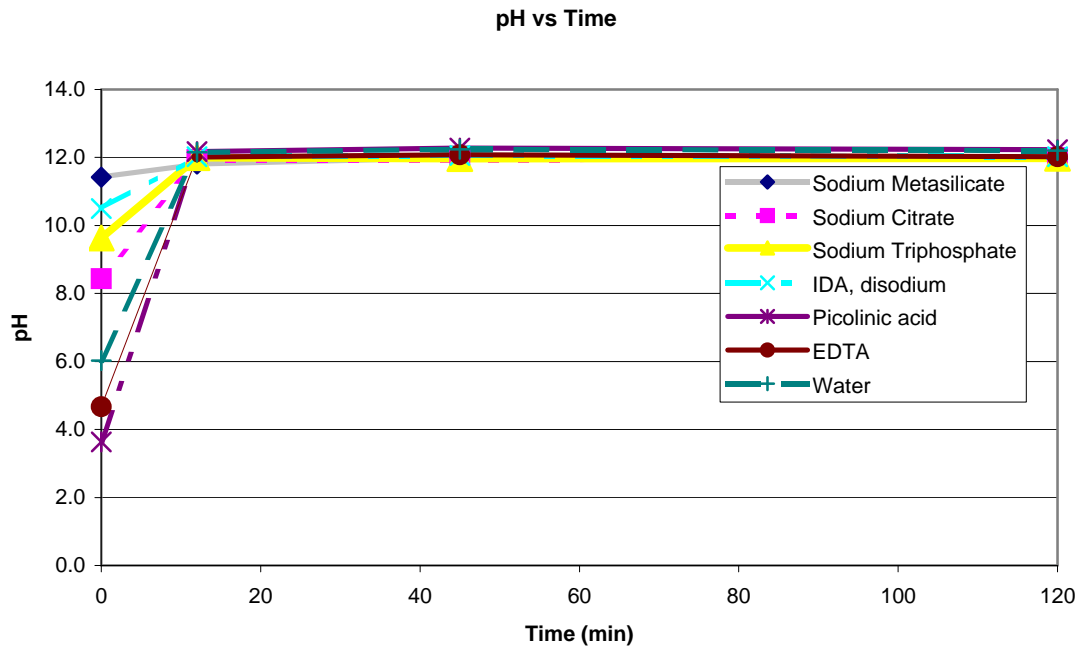


Figure 8: pH vs. time for all chelating agents with $\text{Ca}(\text{OH})_2$ at room temperature and pressure

Effect of pH on the dissolution rate

The pH trends recorded in the first set of experiments prompted the investigation of acidity on the dissolution of the Ca-bearing solids. Three different concentrations of chelating agent solutions were tested with a buffer solution of pH 4.74 and $\text{Ca}(\text{OH})_2$. The objective of this being to determine pH effects on the dissolution rate, especially given the overwhelming causticity with calcium hydroxide. The chosen chelating agents, IDA at 0.02 M and EDTA at 0.02 M and 0.005 M, were tested for the dissolution of $\text{Ca}(\text{OH})_2$. The data is shown in Figure 9. From this graph, it is evident that the pH effect, or acidic effect, dominates the dissolution under given experimental conditions. Moreover, all the samples were completed dissolved at 10 minutes. They were allowed to run for 20 minutes before a final sample was taken, but it did not seem necessary to run for longer. Although water appears to be at a higher level at the final

concentration, this is assumed to not be consequential and only a matter of error in dilution or error due to the instrument, because all material had dissolved in all cases. Thus, the concentration should actually be equivalent for all cases. This discrepancy prompted the move from flame AAS to a more reliable instrument, the ICP OES. The remaining chelating agent data that is presented was obtained using ICP-OES.

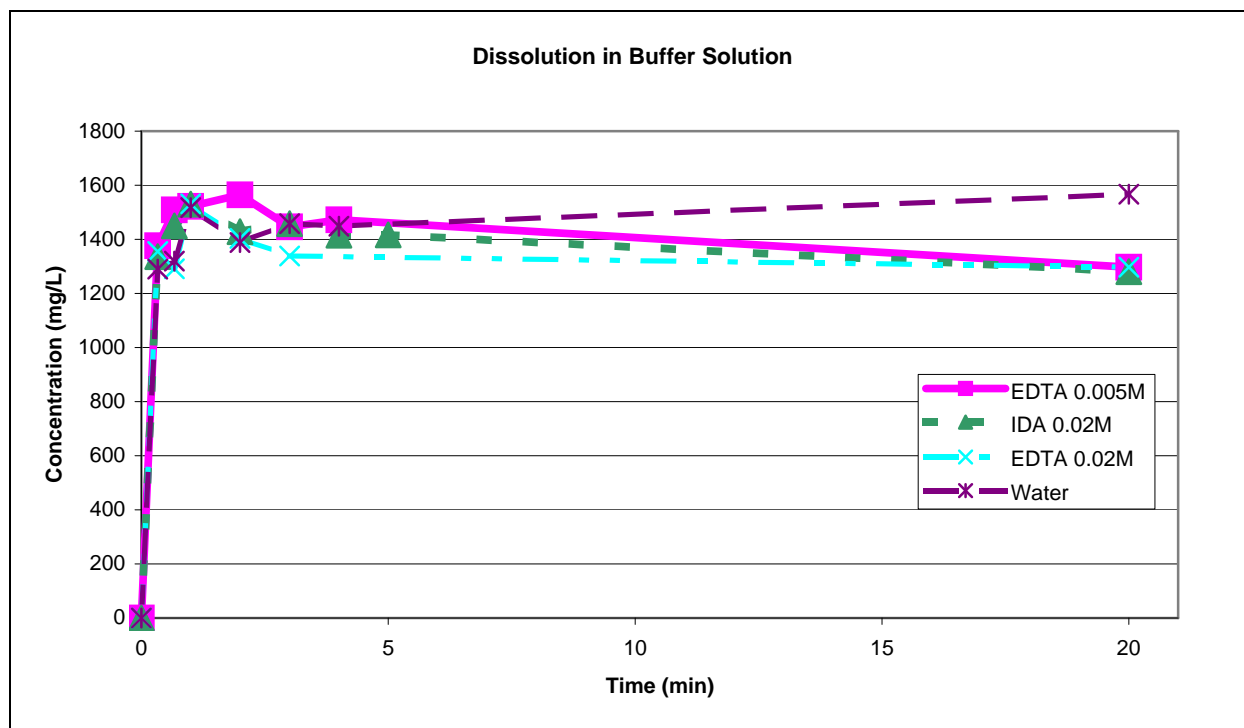


Figure 9: Dissolution of $\text{Ca}(\text{OH})_2$ in acidic buffer solution with EDTA and IDA at room temperature and pressure

Effects of concentration of chelating agents on the dissolution rate

The selected chelating agents, IDA and EDTA, were also tested at different molarities, as explained previously. From Figure 10, it is evident that higher concentration does affect dissolution of calcium hydroxide. Specifically, the highest dissolution rates are seen with 0.02 M EDTA and IDA solution. These solutions have 1176 ppm and 1107 ppm for IDA and EDTA,

respectively. Nevertheless, more work is needed to understand what the optimum molarity would be. Suffice to say that at higher concentrations, more leaching is evident and it is fair to assume that this trend would be observed with other concentrations. Comparison of this data with that from the Flame AAS does show some discrepancy, but this could be a result of errors in dilution, reliability of the instruments, or the difference in the way that the two instruments collect data. The ICP OES has a more rigorous method of data analysis and is also much more reliable.

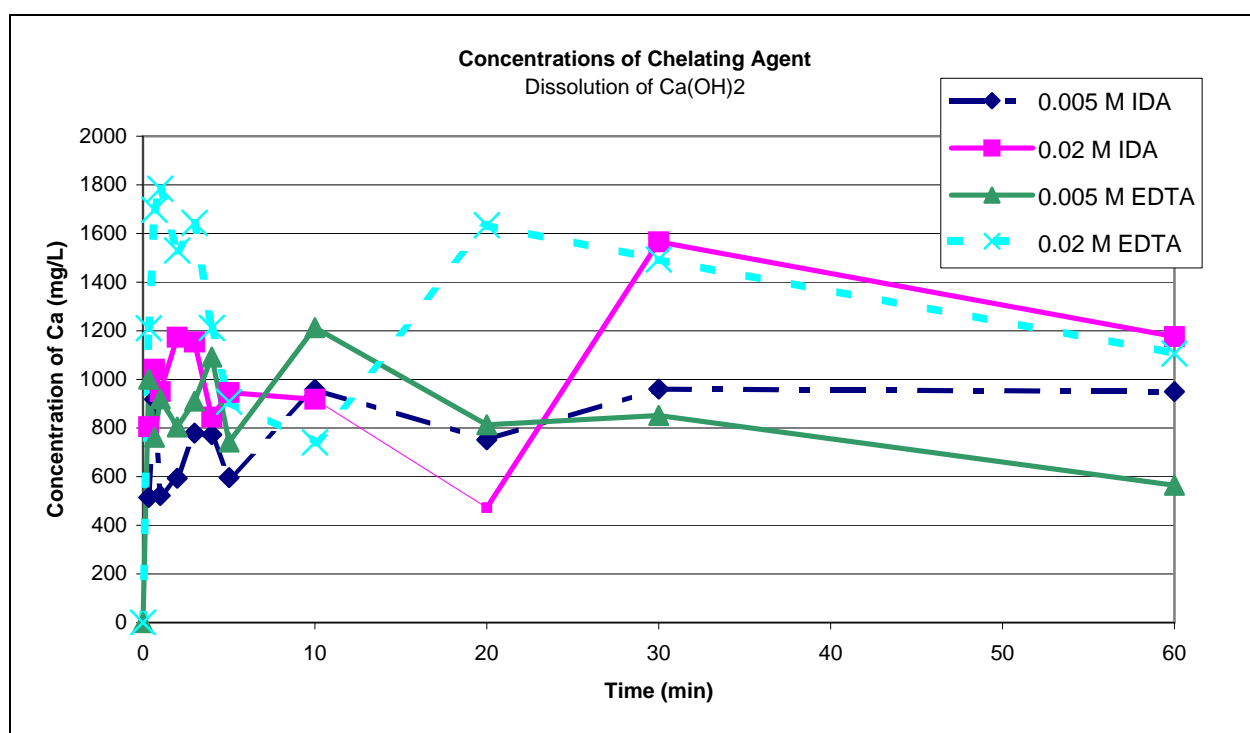


Figure 10: Effects of concentrations of chelating agents with Ca(OH)_2 at room temperature and pressure

Effects of material sensitivity on the dissolution rate

Further analysis focused on leaching of calcium from different starting materials. As described earlier in this chapter, a 0.01 M chelating solution was used of both IDA and EDTA for each type of material – CaCO_3 , CaSO_4 , and FGD solid samples. Figure 11 shows the

dissolution results of pure CaCO_3 . Interestingly, CaCO_3 is leached more easily using EDTA, however the concentration is still fairly low when compared to the dissolution of calcium hydroxide samples, 140 ppm for EDTA with CaCO_3 versus 815 ppm with Ca(OH)_2 . IDA is much lower, with a final value of 17 ppm. In conjunction with these results, future work should focus on the implications of these compounds when precipitating calcium carbonate.

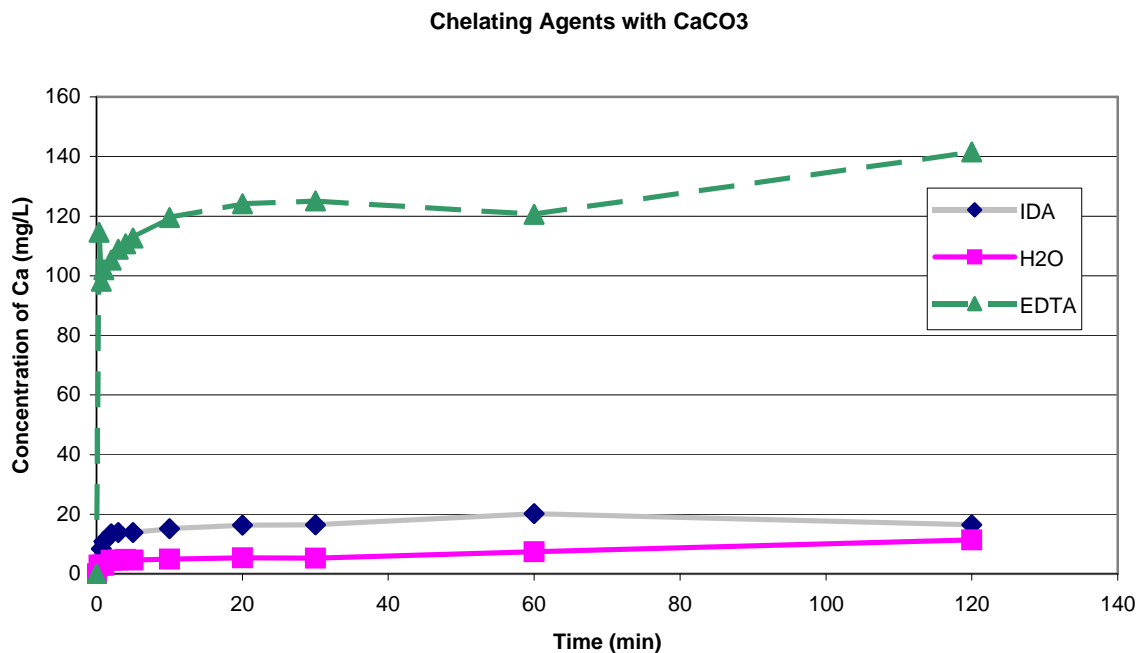


Figure 11: Effects of chelating agents with CaCO_3 at room temperature and pressure

The chelating agents were also used with CaSO_4 to determine the amount of calcium that would be leached from a “stable” product. Ideally, no calcium would be leached from this solid sample, as it is supposed to be an end product of FGD process. In reality, some calcium will leach from solution, thus, water is used as the control baseline. For all three runs, the amount of calcium leached was about the same, so dissolution of sulfate does not appear to be a problem, as shown in Figure 12. From the chelating data previously shown in Table 6, EDTA is a stronger

chelator than sulfate, but IDA is not. This suggests that EDTA should leach some of the sulfate, but experimentally, this was not observed from the amount of calcium in solution. Visually, however, it was observed that the solid changed forms with EDTA, this might have been due to the large particle size of CaSO_4 . The solid changing was not observed in other runs, however, in all cases, the solution became cloudy. The solution was especially cloudy in the case of IDA. Although this may have been a result of the mixing dynamics, it is possible that CaSO_4 , though initially leached out by the chelating agent, forms a more stable complex as sulfate and eventually returns to this form. The dramatic increase in the case of IDA around 30 min could be attributed to a similar phenomenon.

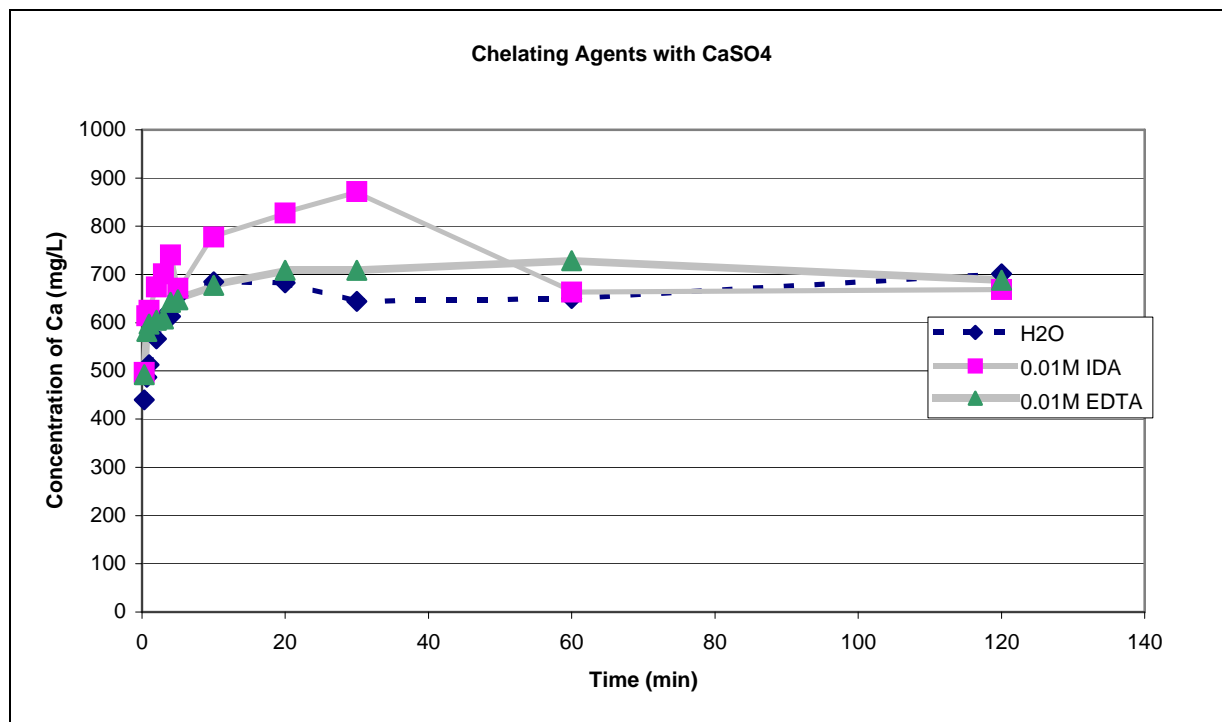


Figure 12: Effects of chelating agents with CaSO_4 at room temperature and pressure

Interestingly, when the chelating agents were used to dissolve FGD material, the results were different, as shown in Figure 13. Given that some of the FGD material is CaSO_4 , it was

expected that the results would be similar to those seen for the sulfate runs. At the same time, there are inert materials present in the FGD that would be included in the 1 g sample. Although the amount of calcium leached by EDTA was about the same as in the sulfate run, the amount of calcium available is not the same. This suggests that EDTA leached calcium from all sources, both oxide and sulfate. The quantity of calcium in IDA and water solutions, on the other hand, was much lower. Given that only about 10 % of the calcium in the sample was in the oxide form, one potential reason for the results would be that the IDA leached only the calcium present as CaO. It is also possible that IDA was more favorably forming complex ions with other metal ions existing in the FGD material compared to calcium ions. This is important incentive to continue evaluating the potential of IDA in the process.

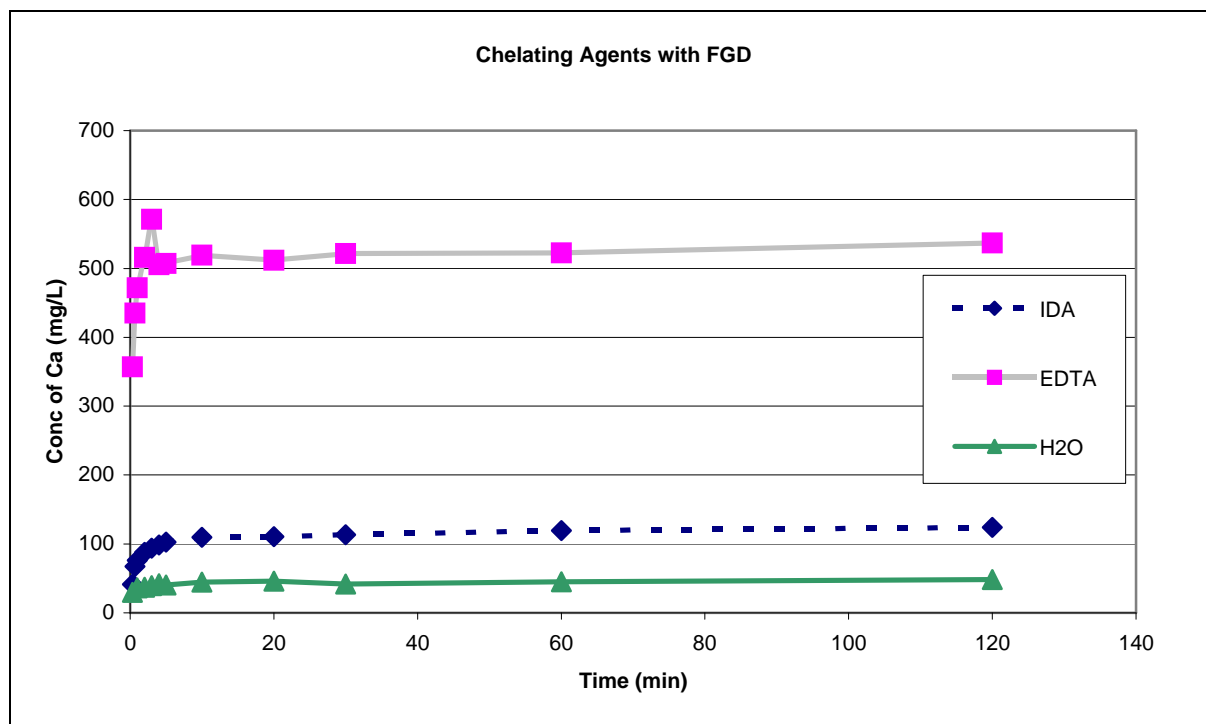


Figure 13: Effects of chelating agents with FGD at room temperature and pressure

4.5 Summary

This chapter presented the work that dealt with evaluation and determination of appropriate chelating agents for calcium reclamation from industrial waste. In the initial screening of six different chelating agents, IDA and EDTA were determined to be the most effective in solution with $\text{Ca}(\text{OH})_2$. Further testing evaluated effects of pH, concentration of ligands, and the sensitivity of materials beyond calcium hydroxide on the dissolution rates of the Ca-bearing solid samples. Major findings included determining that the pH effect dominated the reaction under acidic condition. In fact, the chelating agents were essentially useless at pH 4.4. Concentration of the chelating agent was found to have an impact, but molarity was not perfectly optimized due to limited number of experiments. Evaluation of leaching from different materials provided interesting results. It was determined that IDA was the most promising of the materials. Interestingly, this correlates with the data obtained from Morel's book and presented earlier in the chapter, see Table 5. According to this data, EDTA should form a complex ion with calcium, which is stronger than that with sulfate and carbonate, whereas the formation of the Ca-IDA complex ion is expected to be less strong than the tendency of CaSO_4 and CaCO_3 precipitation. This inference has been corroborated for the most part by the results obtained. In subsequent tests, IDA is evaluated; because it should not affect ability to precipitate a carbonate form in the synthesis of PCC. EDTA, on the other hand, may affect the PCC process, because it is a more stable complex than the carbonate. This investigation of EDTA viability in the process is beyond the scope of this project, but will be evaluated in future work.

CHAPTER 5

SYNTHESIS AND TESTING OF PCC

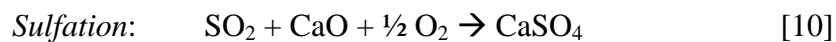
This last section covers the production and characterization of precipitated calcium carbonate (PCC) as a means of testing the viability of the proposed work. The purpose of PCC synthesis is to prove that introduction of a chelating agent to the process does not adversely affect the characteristics of PCC and that supersorbent PCC can indeed be formed.

5.1 Introduction

Previously discussed was the importance of the OSCAR PCC, a supersorbent that has revolutionized the amount of SO_2 that can effectively be separated from a flue gas stream (Gupta and Fan, 2002). Given that the aim of this work is to reclaim calcium from less efficient FGD systems in order to convert it to OSCAR PCC, the most obvious next step is to understand the implications of a chelating agent in the PCC synthesis process. Despite the fact that a chelating agent may successfully leach calcium ions from industrial waste, if it also inhibits the precipitation of calcium carbonate in PCC synthesis, it cannot be considered useful. Successful conversion to OSCAR PCC would be economically worthwhile given that this supersorbent can be injected into the flue gas and does not require a significant amount of initial investment. Moreover, reducing the sorbent requirements of a system will reduce the amount of material in the system, thus saving on both equipment and energy requirements.

Once prepared, OSCAR PCC can be used for both SO_2 capture and CO_2 separation. Depending on whether the PCC is being sulfated or carbonated the reaction is slightly different, but this is only due to the reactant gas. In both cases, the PCC is first brought up to calcination

temperature, 500-900°C, depending on reactant gas, at which point the carbonate is calcined and converted to a highly absorbent CaO product given in Equation (1) from Chapter 1. The calcined particles then react with gaseous SO₂ or CO₂ via the following chemical reactions.



The material produced in carbonation can be regenerated for further utilization, while the sulfate produced is considered an end product.

5.2 Experimental Procedure

In order to test the efficacy of the chelating agent, high surface area precipitated calcium carbonate (PCC) was prepared according to the procedure outlined elsewhere (Gupta and Fan, 2002). A schematic diagram of the slurry bubble column used for PCC synthesis is shown in Figure 14. The carbonator was a 3 ft column with a 1-inch diameter.

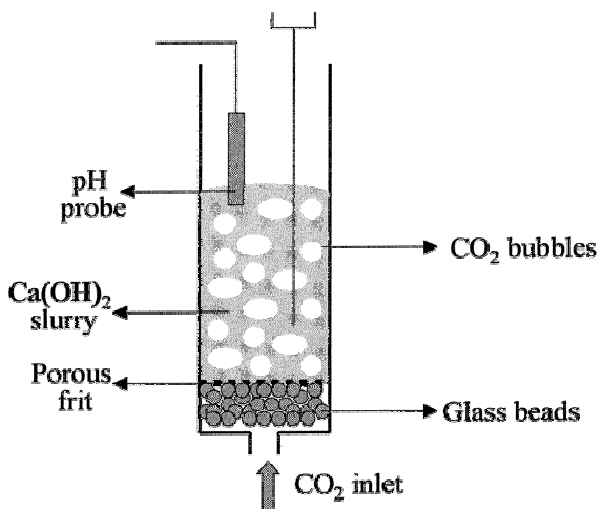


Figure 14 - Schematic diagram of a slurry bubble column used for the synthesis of PCC (Gupta and Fan, 2002)

The components of the slurry used for synthesis of PCC include certified Ca(OH)_2 obtained from FisherChemicals, N40V, a dispersive agent used for pore size modification, obtained from Ciba Specialty Co., and distilled water. In this case, chelating agent was also added to the slurry. In other words, this setting was designed so that both dissolution of Ca-bearing solids and precipitation of calcium carbonate occur simultaneously. The slurry was made up of 0.57 g of IDA, 7.68 g of Ca(OH)_2 , 0.175 g of N40V, and 292 mL of water. The amount of solids used provided a solids loading of 2.56 wt%, which corresponds to 16-sat, i.e. 16 times the saturation limit of Ca(OH)_2 in water. This solids loading amount does not stoichiometrically account for the chelating agent, IDA, which was used at 0.01 M.

The dissolution of calcium hydroxide in the water provided an initial pH of 12. CO_2 gas was then bubbled through the slurry until the solution reached and maintained a pH of 6.0. This pH indicated complete carbonation of calcium ions. The solids were then separated from the liquid using vacuum filtration and then dried at 100°C for a couple of hours.

A second test was conducted using FGD as the Ca-bearing material. In order to account for only 10 % calcium content, the amount of FGD was increased to 28.3 g. Given the fact that FGD does not dissociate to form a high pH in the way that Ca(OH)_2 does, the change in pH was difficult to anticipate. Consequently, the slurry was carbonated for a period of 30 minutes and pH was measured over the course of that period. Following carbonation, the solids were vacuum filtered and dried, only the top portion of the solids were used for analysis as the bottom section of the “carbonator” was made up of mostly inert material, i.e. heavier sandy material. It was determined that more indicative data would be obtained from the “reacted” portion of the material. The same procedure was followed using FGD both with and without chelating agent at a molarity of 0.01.

5.3 Results and Discussion

The PCC generation followed the same procedure as outlined in previous work by the group (Gupta and Fan, 2002). The experimental runs followed the same type of process but had to be modified for generation of PCC from FGD. As previously mentioned, this slurry was carbonated for 30 min and the pH was measured intermittently. Figure 15 shows the pH of the slurry over the course of PCC generation from FGD both with and without IDA.

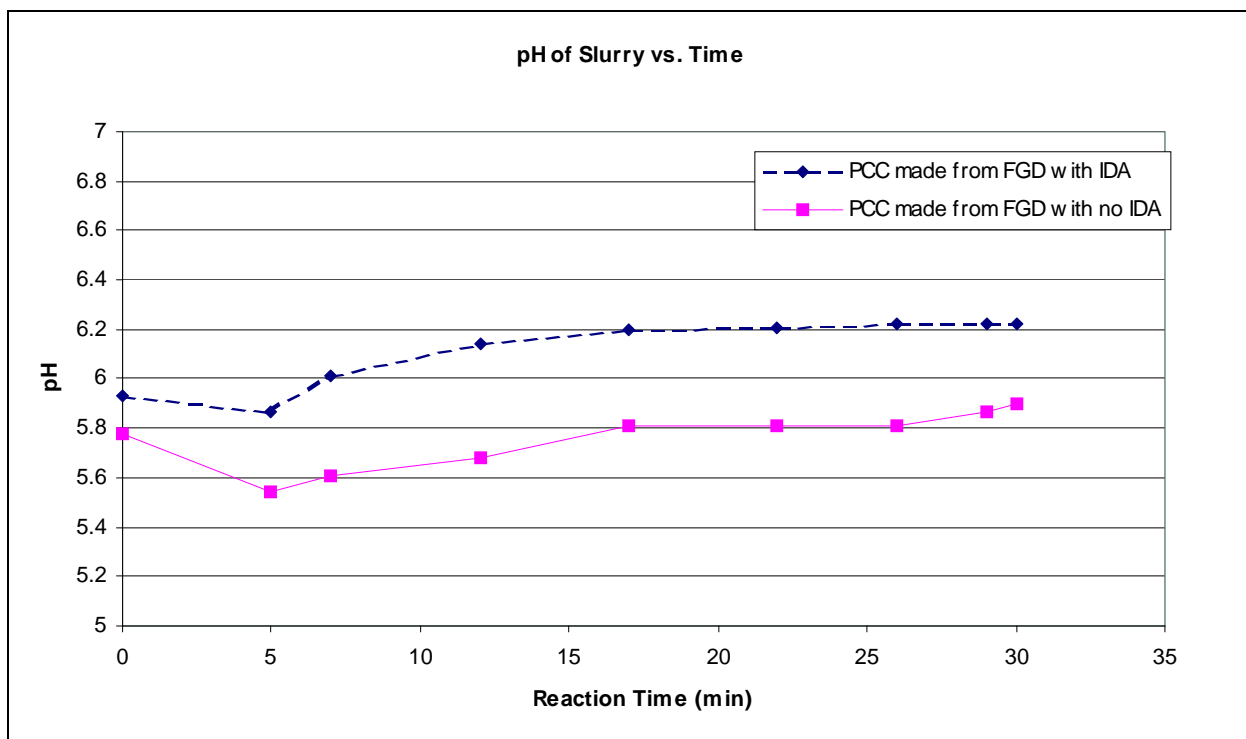


Figure 15: Change of slurry pH over course of reaction, PCC generation from FGD

The change in pH shown in Figure 15 is very slight. Interestingly, the pH with IDA is higher than that without IDA. This suggests that the IDA is capable of leaching some Ca ions into solution. The remaining oxide portion of the compound, though not basic, is capable of neutralizing the acidic pH. The pH, in both cases, increases and levels off as the CO₂ dissolved in

solution forms carbonate compounds. Higher levels of dissolved CO_2 would cause the solution to be acidic. Unlike the immediate carbonation observed in Ca(OH)_2 , the carbonation in FGD was not immediate.

The properties of the PCC generated were evaluated using various analysis techniques, including XRD, SEM imaging, TGA, and BET. XRD was used to determine the composition of the samples. SEM images allowed for the comparison and evaluation of physical structure of the samples. TGA was used to quantitatively measure the change in mass of the sample and correlate this to sulfation or carbonation rates. BET analysis allowed for determination of surface area and pore size.

The XRD spectrum for PCC made from calcium hydroxide with IDA is shown in Figure 16. From this figure, it is apparent that calcium carbonate was the predominant product formed. The spectrum of the sample is shown as a black solid line while the bullet pointed lines indicate the typical spectrum for calcium carbonate. As is typical for PCC analysis, the sample was analyzed from a 2θ value of 10° to 80° .

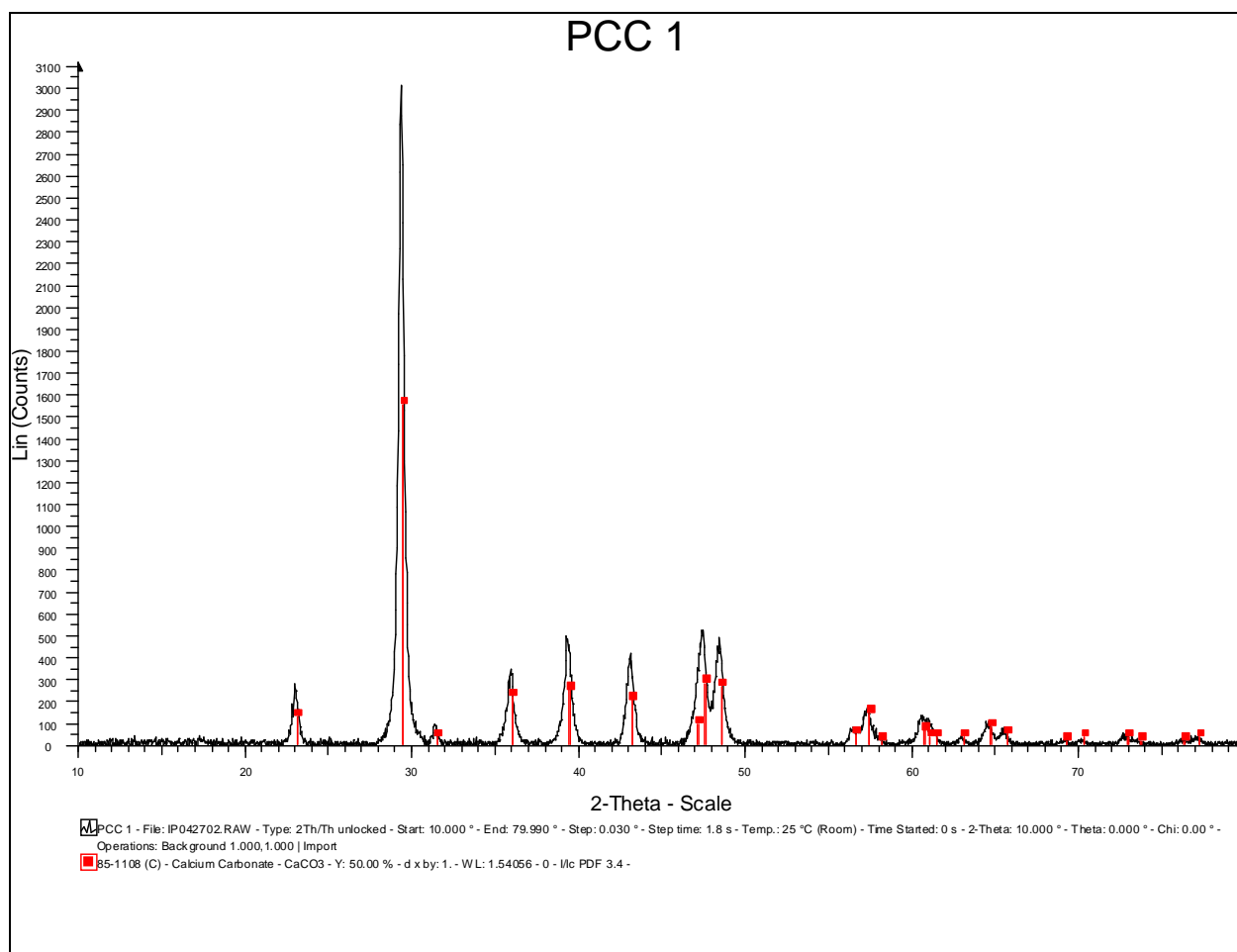


Figure 16: XRD spectrum for PCC made from $\text{Ca}(\text{OH})_2$ with IDA

The XRD spectrum for PCC made from FGD with IDA is shown in Figure 17. Given the make-up of the initial sample, i.e. mostly calcium sulfate, it is not surprising that the XRD of the “PCC product” is still for the most part calcium sulfate. There is no obvious deviation from the spectrum for CaSO_4 , except some of the smaller peaks in the 2θ range from 70 to 80°. Referring back to the CaCO_3 previously shown, it is possible that these small peaks are indicative of some carbonate formation. Figure 18 shows the spectra for PCC made from FGD without IDA. Unsurprisingly, this looks very similar to the Figure 17, as both products come from FGD. The

aforementioned “carbonate” peaks are also present in this spectrum, though they are slightly less pronounced.

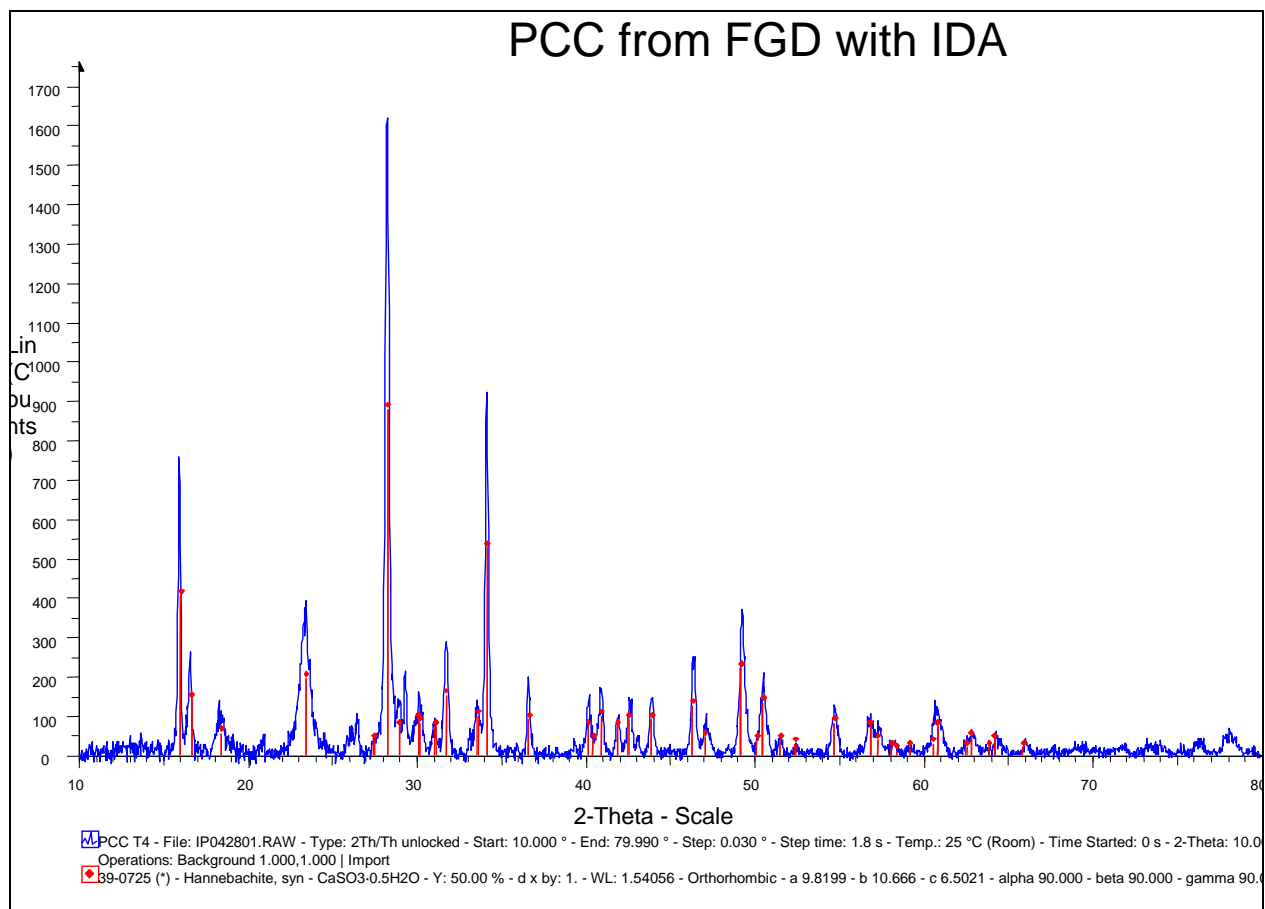


Figure 17: XRD spectrum for PCC made from FGD with IDA

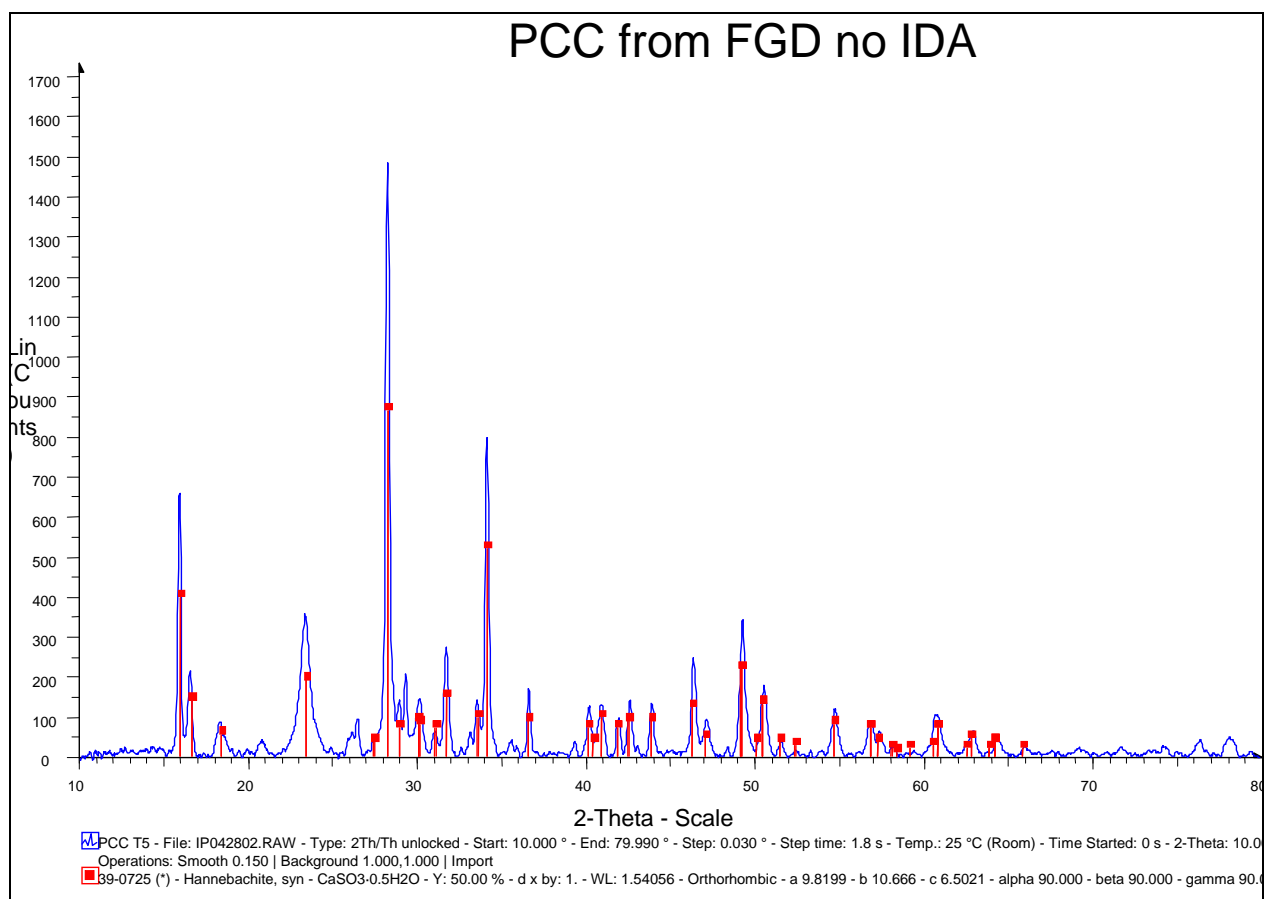
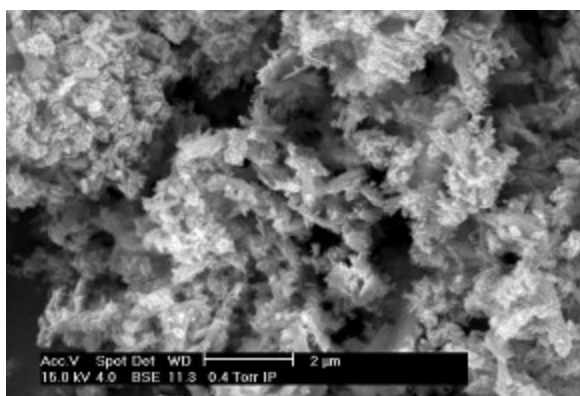
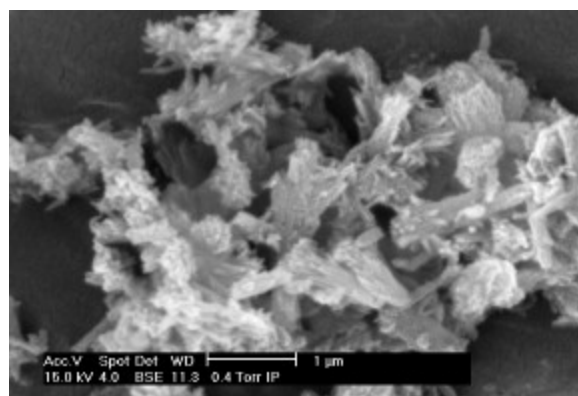


Figure 18: XRD spectrum for PCC made from FGD without IDA

Figures 19, 20, and 21 show SEM images of the various PCC products. The first product, made from $\text{Ca}(\text{OH})_2$ is shown in Figure 19 and is similar to the structure expected for PCC. At 2 μm , shown in Figure 19 (a) the surface appears rough and with high surface area. A slightly higher magnification, shown in Figure 19 (b), reveals the intricate pore structure of the material. Figure 20 shows the structure of the PCC product from FGD with IDA. This material has retained some of the plate-like structures observed in the procured FGD material, however, there is evidence of some pore development. The possible carbonation is circled in Figure 20 (b). The product shown in Figure 21 is from FGD without IDA. The structure is very similar to that of the original FGD material and did not appear to contain the pore development of the product with IDA.

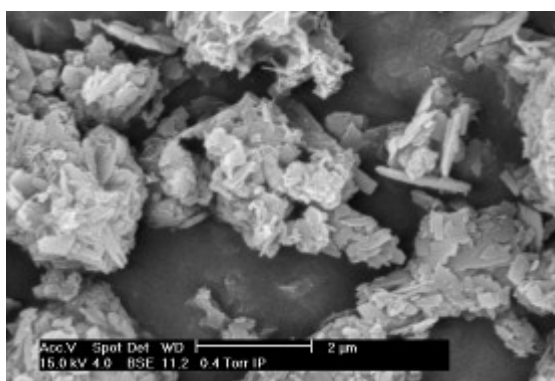


(a)

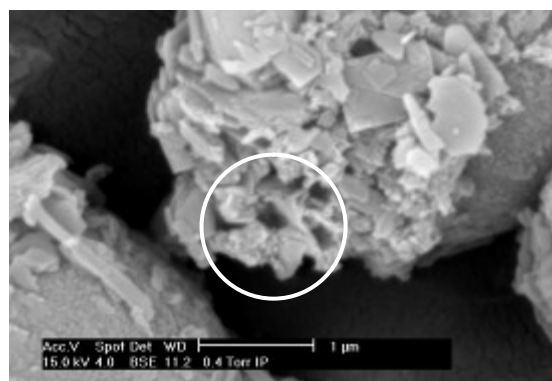


(b)

Figure 19: SEM images of PCC made from $\text{Ca}(\text{OH})_2$ with IDA at (a) 2 μm and (b) 1 μm

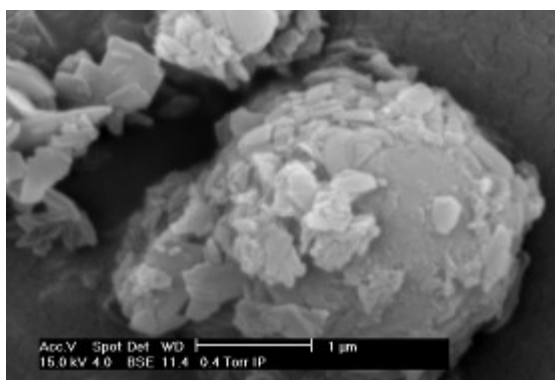


(a)

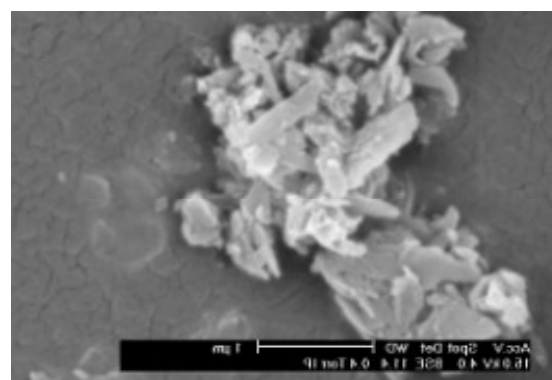


(b)

Figure 20: SEM images of PCC made from FGD with IDA at (a) 2 μm and (b) 1 μm



(a)



(b)

Figure 21: SEM images of PCC made from FGD without IDA at 1 μm

BET analysis confirmed that the PCC synthesized with IDA was similar to typical OSCAR PCC. A typical PCC has a surface area of $49.2 \text{ m}^2/\text{g}$ (Iyer et al., 2004). PCC with IDA had a larger surface area at $64.3 \text{ m}^2/\text{g}$. Both samples of PCC synthesized from FGD had a higher surface area than FGD, but this data was not conclusive as PCC from FGD with IDA had a surface area of $22.1 \text{ m}^2/\text{g}$ while PCC from FGD without IDA had a surface area of $22.9 \text{ m}^2/\text{g}$. The original FGD sample had a surface area of only $15.4 \text{ m}^2/\text{g}$. A useful measurement for future work would be the analysis of pore size.

TGA data for the PCC made from $\text{Ca}(\text{OH})_2$ with chelating agent shows that effectiveness is not inhibited by the addition of IDA to the slurry. The calcination-sulfation cycle, shown in Figure 22, is comparable to results previously reported for high reactivity PCC, capable of achieving approximately 70 % conversion (Fan and Jadhav, 2002). The calcination-carbonation cycle, shown in Figure 23, shows conversion for precipitated PCC with high pore volume and results are those previously obtained by the group for high reactivity PCC. In previous work performed by the group the conversion of PCC was found to be greater than 80 % (Iyer et al., 2004). This is similar to the results shown here. This suggests that the performance of PCC is not hindered by the presence of IDA in the slurry. The arrows in Figures 22 and 23 indicate the point at which the gas was switched to SO_2 and CO_2 , respectively. From the figures, it is clear that sulfation and carbonation both began upon introduction of the reactant gas. Each weight change corresponds to the extent of each reaction: calcinations, sulfation and carbonation.

Based on the results shown in Figures 22 and 23, the extents of those reactions with respect to the theoretical values are calculated from an equation for the conversion of CaO towards sulfation and carbonation, defined as:

$$\text{Conversion} = \frac{\text{Observed Weight Increase of CaO}}{\text{Theoretical Maximum Increase in Weight Possible}}$$

The theoretical maximum increase for sulfation corresponds to the initial weight of CaO, upon injection of reactant gas times 2.429. The theoretical maximum increase for carbonation uses a multiplicative factor of 1.786 times the initial weight of CaO. The maximum conversions for sulfation and carbonation are found to be 76 % and 67 %, respectively.

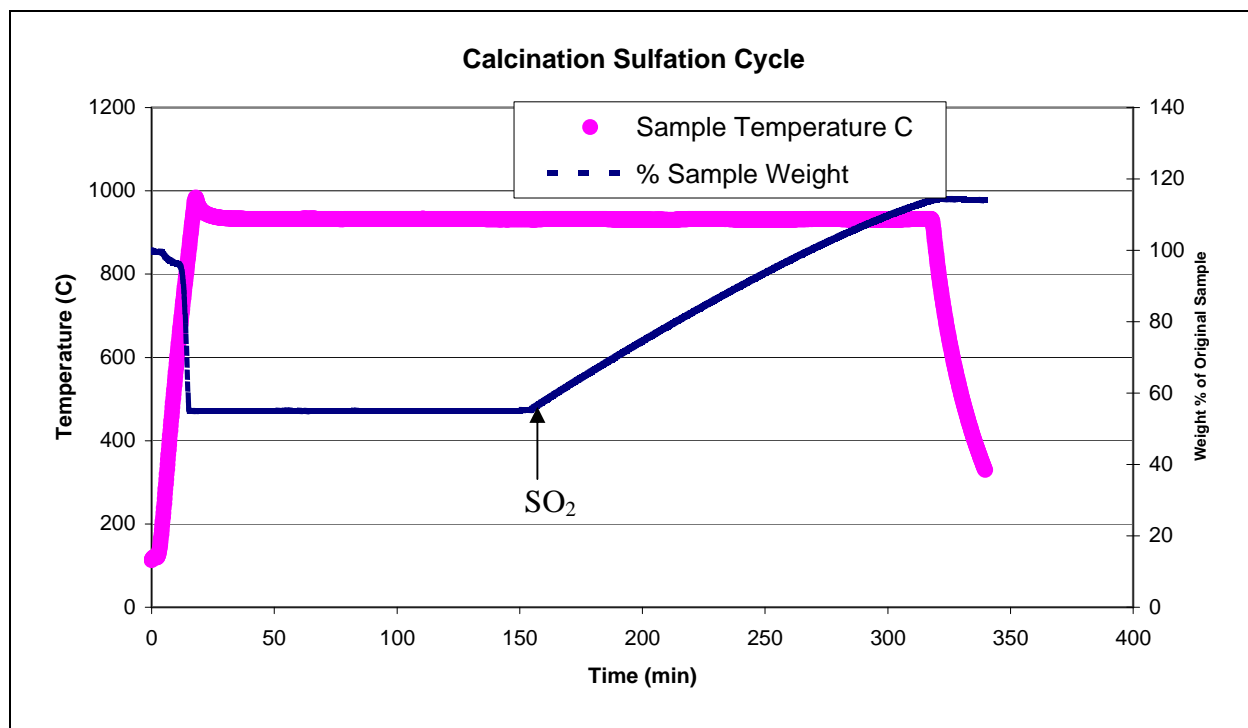


Figure 22: Calcination and sulfation of PCC made from $\text{Ca}(\text{OH})_2$

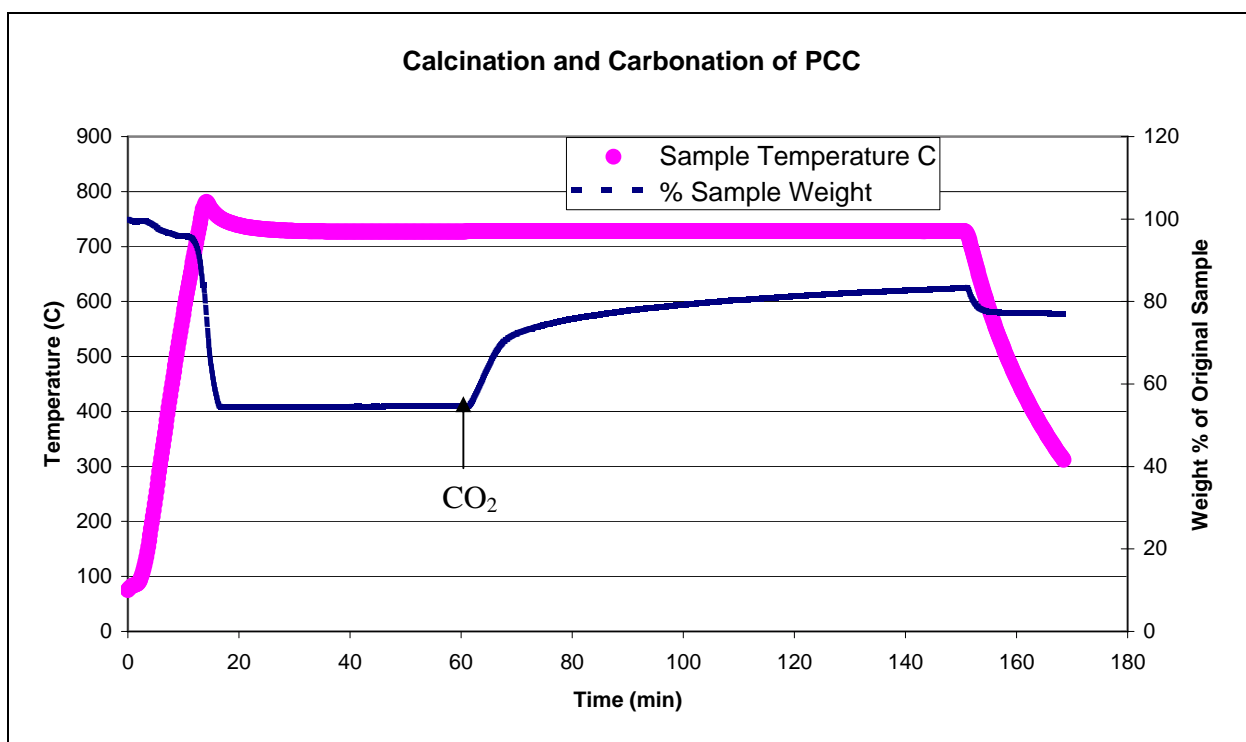


Figure 23: Calcination and carbonation of PCC made from $\text{Ca}(\text{OH})_2$

5.4 Summary

This chapter explained the process of synthesizing and testing PCC made with and without a chelating agent, IDA. The PCC synthesis process was slightly modified to produce PCC from FGD solid sample, because of the small amount of calcium in this material. The PCC generated in the normal fashion with calcium hydroxide and IDA (as an additive) exhibited the typical properties of OSCAR PCC, suggesting that IDA does not inhibit either the precipitation of calcium carbonate, or the subsequent reactions, sulfation or carbonation, of the PCC. Future work should examine more closely the properties of PCC generated from $\text{Ca}(\text{OH})_2$ with different chelating agents and of PCC generated from various Ca-bearing industrial waste products with chelating agents. Another important next step of this work will be to analyze the effects that a chelating agent has on the multi-cyclic carbonation-calcination capabilities of PCC previously demonstrated by the group.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

In this work, Ca-bearing industrial waste by-products were procured and characterized. Given the compositions, and, more specifically the quantity of reclaimable calcium, the most viable products were those from flue gas desulfurization sources. The objective was to reclaim calcium from industrial waste sources and use the calcium as a raw material for supersorbent OSCAR PCC. This type of sorbent is particularly interesting, not only because of its high reactivity but also because it can be directly injected into the flue gas and requires no large capital equipment. The overarching implications of this calcium reclamation would be to reduce the material flow through the system and reduce the amount of calcium-based sorbent required in SO₂ control processes. The calcium could also potentially be reused as an effective sorbent for capturing CO₂ in a flue gas stream.

It was shown that calcium could be reclaimed, at least to some degree, from industrial waste, specifically FGD materials, using chelating agents. The work used a number of Ca-bearing materials to understand and quantify the dissolution properties of multiple chelating agents. Both EDTA and IDA were determined to be the effective complexing agents with calcium. IDA, however, was selected for use in further testing of PCC generation, because it did not appear to dissolve CaCO₃, and, thus, was not considered a threat to the precipitation step of the PCC synthesis process. PCC generated with IDA did not seem to be hindered in either the calcination-sulfation or calcination-carbonation process and had similar structural properties to the OSCAR PCC previously documented by the group.

Future initiatives should examine the trade-offs associated with using EDTA or IDA and the effects that the choice of chelating agent has on eventual yield of PCC. Whether this process is hindered by calcium dissolution kinetics or calcium carbonate precipitation should be documented. Furthermore, the products generated from industrial wastes should be further analyzed. Specifically, future work should examine the extent of the usability of PCC obtained from industrial wastes and work should be done to characterize their performance in calcination-sulfation and multi-cyclic calcination-carbonation studies. Although the solid waste from the dry FGD process is expected to have the highest calcium content, unfortunately it was very difficult to collect this sample from industry. Thus, the dry FGD solid samples should be procured and tested following this study for evaluation in future work.

REFERENCES

- 2004 *Coal Combustion Product (CCP) Production and Use Survey*. American Coal Ash Association: Aurora, CO, 2005.
- Brown, T. L., LeMay, H. E. Jr., and Bursten, B. E., *Chemistry The Central Science*, 5th ed., Prentice-Hall, Inc.: New Jersey, 1991.
- Chong, T.H., and Sheikholeslami, R., "Thermodynamic and Kinetics for Mixed Calcium Carbonate and Calcium Sulfate Precipitation," *Chem. Eng. Sci.*, 56, 5391-5400, 2001.
- Dry Flue Gas Desulfurization Technology Evaluation*, Project Number 11311-000 Prepared for National Lime Association [Report Online]. Sargent and Lundy, LLC: Chicago, IL, 2002. Available at: <http://www.lime.org/NLADryFGD.pdf>. Accessed: February 20, 2006.
- Fredd, C. N., and Fogler, H. S., "The Influence of Chelating Agents on the Kinetics of Calcite Dissolution," *Journal of Colloid and Interface Science*, 204, 187-197, 1998.
- Friis, A. K., Davis, T. A., Figueira, M. M., Paquette, J., and Mucci, A., "Influence of *Bacillus subtilis* Cell Walls and EDTA on Calcite Dissolution Rates and Crystal Surface Features," *Environ Sci Technol.* 37, 2376-2382, 2003.
- Gupta, H., and Fan, L.-S., "Carbonation-Calcination Using High Reactivity Calcium Oxide for Carbon Dioxide Separation from Flue Gas," *Ind. Eng. Chem. Res.* 41, 4035-4042, 2002.
- Iyer, M. V., Gupta, H., Sakadjian, B. B., and Fan L.-S., "Multicyclic Study on the Simultaneous Carbonation and Sulfation of High Reactivity CaO: Effect of Residence Time on Selectivity," *Ind. Eng. Chem. Res.*, 43, 3939-3947, 2004.
- MacAdam, J., and Parsons, S. A., "Calcium carbonate scale formation and control," *Reviews in Environmental Science and Bio/Technology*, 3, 159-169, 2004.
- Manahan, S. E., *Environmental Chemistry*, 7th ed., Lewis Publishers: Boca Raton, FL, 2000.
- Morel, F. M. M. *Principles of Aquatic Chemistry*, John Wiley and Sons: New York, NY, 241-251, 1983.
- Perry, T. D. IV., Duckworth, O. W., Kendall, T. A., Martin, S. T., and Mitchell, R., "Chelating Ligand Alters the Microscopic Mechanism of Mineral Dissolution," *J Am Chem Soc.*, 127, 5744-5745, 2005.
- Sillanpaa, M., Orama, M., Ramo, J., Oikari, A., "The Importance of Ligand Speciation in Environmental Research: A Case Study," *Sci Total Environ.*, 267, 23-31, 2001.

User Guidelines for Waste and Byproduct Materials in Pavement Construction. Federal Highway Administration. Turner - Fairbank Highway Research Center (TFHRC) Web site. Available at: <http://www.tfhrc.gov/hnr20/recycle/waste/begin.htm>. Accessed 12/13/2005.

United States Department of Energy (US DOE) Web site. *Carbon Capture Research*, Available at: <http://www.fossil.energy.gov/programs/sequestration/capture/>. Accessed 5/1/2006.

United States Environmental Protection Agency Web site. *Air Trends - More Details on Sulfur Dioxide - Based on Data Through 2002*, Available at: <http://www.epa.gov/airtrends/sulfur2.html>. Accessed 5/1/2006.

United States Environmental Protection Agency Web site. *Module 6: Air Pollutants and Control Techniques - Sulfur Oxides*, Available at: <http://www.epa.gov/eogapti1/module6/sulfur/control/control.htm>. Last updated 3/2/2006.

Westin, K. J., and Rasmuson, A. C., "Precipitation of Calcium Carbonate in the Presence of Citrate and EDTA," *Desalination*, 159, 107-118, 2003.

Wet Flue Gas Desulfurization Technology Evaluation, Project Number 11311-000 Prepared for National Lime Association [Report Online]. Sargent and Lundy, LLC: Chicago, IL, 2003. Available at: http://www.lime.org/Wet_FGD.pdf. Accessed February 20, 2006.

This document was created with Win2PDF available at <http://www.daneprairie.com>.
The unregistered version of Win2PDF is for evaluation or non-commercial use only.